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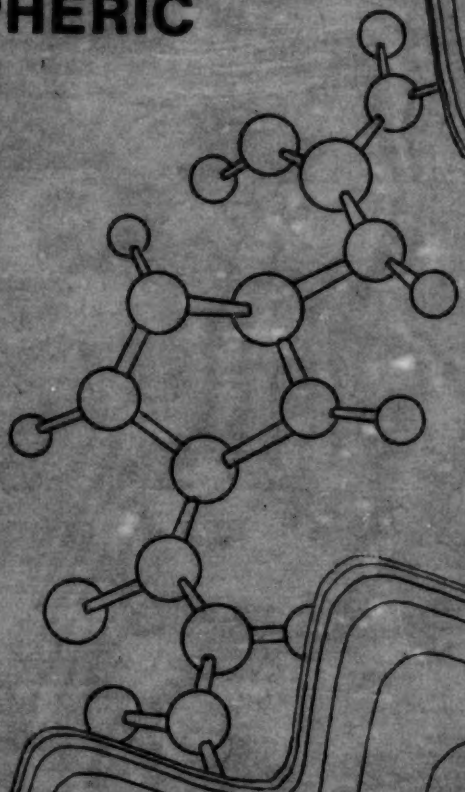
CHEMICAL & ATMOSPHERIC SCIENCES



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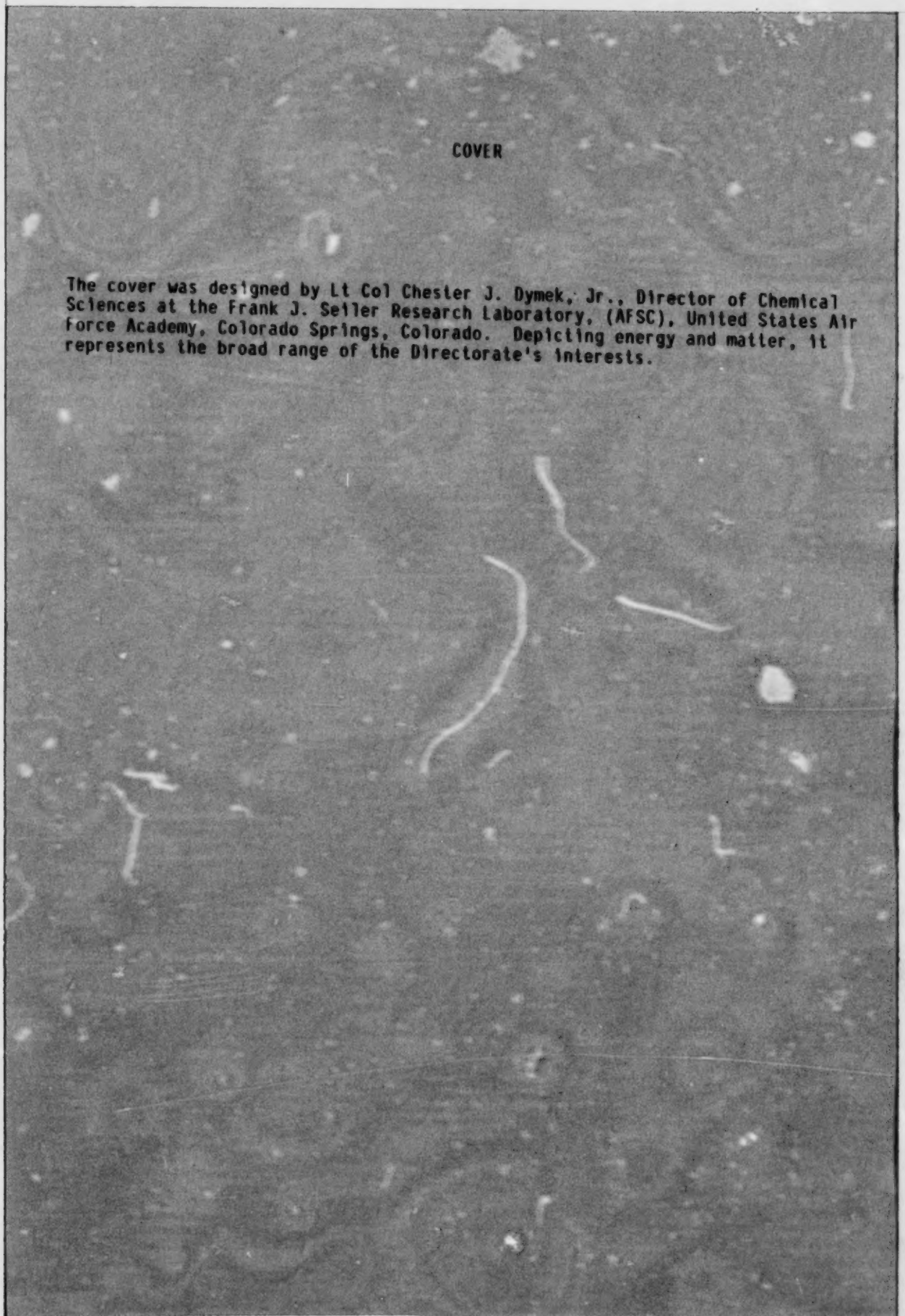

COVER

The cover was designed by Lt Col Chester J. Dymek, Jr., Director of Chemical Sciences at the Frank J. Seiler Research Laboratory, (AFSC), United States Air Force Academy, Colorado Springs, Colorado. Depicting energy and matter, it represents the broad range of the Directorate's interests.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

18. Subject Terms (Continued)
Atmospheric Sciences Mesoscale Weather Forecasting Cloud Physics
Radar Atmospheric Research Upper Atmosphere

A review is presented of research efforts sponsored by the Directorate of Chemical and Atmospheric Sciences which have completed their period of support. Illustrated accounts resulting from the basic research programs in the Atmospheric and Chemical Sciences are highlighted. The Atmospheric Science is concerned with meteorology and upper atmospheric structure and dynamics. The meteorology focuses on mesoscale meteorology, cloud physics, and atmospheric dynamics. The Chemical Sciences deal with chemical techniques, chemical structures, surface chemistry, chemical dynamics, and synthesis and properties of materials.

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29TH AFOSR

CHEMICAL AND ATMOSPHERIC SCIENCES

PROGRAM REVIEW

FY84

LARRY P. DAVIS, EDITOR

EUNICE L. LUTHER, MANAGING EDITOR

SEPTEMBER, 1985

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)

DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES

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Atmospheric Sciences 105

DEDICATION

DENTON W. ELLIOTT

Denton W. Elliott was appointed to the Chemistry Staff of OSR in August 1952 as a Research Administrator. He brought with him a varied teaching and industrial experience, interrupted by 3 years as an Officer in the U.S. Navy during World War II.

When Denny Elliott retired in January, 1985, he was the Assistant Director of Chemical and Atmospheric Sciences, AFOSR. As such he shared responsibility in the administrative and technical affairs of the Directorate of Chemical and Atmospheric Sciences. These included planning, selecting, and managing a grant and contract program in basic chemical research areas of interest to the long range mission of the Air Force and involved interpreting chemical research accomplishments for maximum benefit to the Air Force of the future.

Denny Elliott was born and brought up in central Ohio. He attended high school in the village of Canal Winchester and worked his way through Otterbein College, from which he received his Bachelor's degree in 1937. He was quite active in campus activities. He was a member of the basketball and baseball teams, participated in the dramatic and forensic societies, was president of the student council and the Junior Class, was listed in "Who's Who in American Colleges and Universities" and was selected Outstanding Senior by Sigma Delta Phi.

After graduation he spent the next five years teaching science and coaching in Ohio high schools. During the summers he took graduate work at Ohio State University, from which he received his Masters degree in Education in 1947.

From summer of 1942 to August 1943 he was employed as a supervisor and analytical chemist in an explosives plant which was making fuzes and boosters for 105-inch shells and two-ton bombs.

In July 1943 Denny received a Commission as Ensign in the U.S. Navy. After three months of indoctrination courses at Cornell University, he was assigned as Engineering Officer on a destroyer, the USS WOODWORTH. While on this ship, he participated in several air and sea encounters with the Japanese in and around Guadalcanal; among them was the first destroyer raid on Rabaul. This ship also had the honor of escorting the USS BALTIMORE with President Roosevelt aboard to visit Pacific installations. In early 1944, when new ships were being assigned to the Pacific, Denny was transferred to the USS STAFFORD as Gunnery Officer. This destroyer operated with aircraft carriers in "hunter-killer" groups to seek out and destroy enemy submarines. The ship took part in the landing on the Philippines with the return of Gen. MacArthur, at which time the STAFFORD was disabled, due to a hit by a kamikaze. The ship returned to the States for repair and was reassigned to the Okinawa area prior to the end of the war.

Denny returned to civilian life after the war. He attended Ohio State graduate school until September 1946, at which time he accepted a position

with Champlain College, Associated Colleges of Upper New York, as instructor in Chemistry. He helped set up the Department and taught general chemistry, analytical chemistry, and an instrumental course for seniors. In 1951 - 1952 he acted in part-time capacity as Assistant to the Dean of Academic Administration. He did graduate study at Columbia University during the summers of 1951 and 1952. After joining the Office of Scientific Research in the fall of 1952, he entered The Johns Hopkins University on a part-time basis and pursued course work toward the Ph.D. in Chemistry.

In time of service Denny Elliott is one of the three or four individuals who had been with the Office of Scientific Research almost from its inception. The experience which he has gained over the growth period of support for chemistry research has been most valuable to AFOSR and to the Air Force. His experience and many contributions will be sorely missed by the Directorate. As we honor him by this dedication, we wish him well in his retirement.

EDITORS' FOREWORD

We are especially pleasd to dedicate this Review to Denton Elliott upon his retirement from AFOSR. He made many outstanding contributions to the AFOSR Chemistry program. The format of the 29th edition of the Chemical and Atmospheric Sciences Review is similar to that of the 28th edition. Included is a short assessment of each program area each by program manager. We have organized the active research programs and completed project summaries by program area. This will help users of the review locate material most relevant to their interests. We invite your comments and suggestions on methods to improve our Chemical and Atmospheric Sciences Review. A copy of AFSC Form 459 is included inside the front cover for this purpose.

The editors wish to thank all of the Directorate of Chemical and Atmospheric Sciences staff for their assistance in preparing this document. In particular, the editors would like to thank three of the new program managers, Dr. Frank Wodarczyk, Major Larry Burggraf, and Dr. John Wilkes, who helped summarize program areas for program managers who have since left AFOSR. In addition, Major James I. Metcalf, USAF Reserve, did an outstanding job of proofreading major parts of the manuscript. Special thanks go to our secretarial staff for the long hours and dedication to completion of this year's review.

Larry P. Davis

Larry P. Davis

Eunice L. Luther

Eunice L. Luther

MISSION

The Directorate of Chemical and Atmospheric Sciences of the Air Force Office of Scientific Research has the mission to encourage and support fundamental research designed to increase knowledge and understanding, to stimulate the recognition of new concepts, and to provide for early exploitation by defense technology.

The Directorate obtains and maintains for the Air Force a diversified program of research at in-house laboratories as well as extramurally at university and industrial laboratories. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways, the Directorate helps the Air Force maintain technological superiority.

October 1985

TO: FRIENDS OF AFOSR

The preparation and publication of this annual report represents a major investment of time and energy by the Directorate staff. We consider it time well spent and that we have a responsibility to advise the scientific public of our planned areas of research emphasis as well as past successes. We ask for your help in assuring that the limited number of copies of this report reach the hands of those interested in it. Your prompt return of the enclosed survey card will assure your continued receipt of future editions (if you wish it). If we do not hear from you, we will conclude that your place on the mailing list can be yielded to someone else.

Sincerely

Donald L. Ball

DONALD L. BALL
Director of Chemical and
Atmospheric Sciences

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Operating under contract F49620-84-C-0073 with Georgetown University
Principal Investigator: Professor Joseph E. Earley
Department of Chemistry
Georgetown University
Washington, D.C. 20057

CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 84 with funds provided in part or wholly by the Directorate of Chemical and Atmospheric Sciences as a means of furthering areas of scientific research of particular interest to the Air Force.

Alaska Workshop on Gravity Waves and
Turbulence in the Middle Atmosphere
Dr. David C. Fritts
University of Alaska
Fairbanks, AK
18-22 July 83

Catalytic Reaction Mechanism: The Role of
Surface Structure and Composition
Materials Research Society
Boston, MA
14-16 November 1983

Ordered Polymers Workshop
Dr. Wiff
University of Dayton
Dayton, OH
16-18 November 1983

International Conference on Radiationless Transitions
Dr. E.K.C. Lee & Dr. F. S. Rowland
University of Calfornia
Newport Beach, CA
3-7 January 1984

Gordon Research Conference on Electrochemistry
Dr. Larry Faulkner
University of Rhode Island
Santa Barbara, CA
22-27 January 1984

1984 Symposium on Better Ceramics through Chemistry
Dr. David Clark & Dr. C. Jeff Brinker
Materials Research Society
Albuquerque, NM
27-29 February 1984

Workshop and Design Study on Measurement of
Horizontal Structures and Wavelengths (5-500 km)
in Mesopheric Gravity Waves, Tides, and Winds
Dr. Gene W. Adams
Center for Atmospheric and Space Sciences
Utah State Unversity
Logan, UT
21-25 May 1984

Seventh International Conference on Atmospheric Electricity
Dr. Volker A. Mohnen
Atmospheric Sciences Research Center
State University of New York at Albany
Albany, NY
4-8 June 1984

Sixth Symposium on Applied Surface Analysis
Dr. John T. Grant
University of Dayton
Dayton, OH
6-8 June 1984

Gordon Research Conference on Liquid Crystal Polymers
Dr. Robert W. Lenz
University of Rhode Island
Colby-Sawyer College
New London, NH
9-13 July 1984

Workshop on the Chemical Processing of Structural Ceramics
for Use in Severe Environments
Dr. Norman Hecht
University of Dayton
Hueston Woods State Park Lodge, OH
16-18 July 1984

Gordon Research Conference on Electron Spectroscopy
Dr. C. R. Brundle & Dr. J. L. Dehman
University of Rhode Island
Brewster Academy
Wolfeboro, NH
16-20 July 1984

XXIII International Conference on Coordination Chemistry
Dr. Robert E. Sievers
University of Colorado
Boulder, CO
29 July - 3 August 1984

1984 Gordon Research Conference on Inorganic Chemistry
Dr. Guido Pez
Brewster Academy
Wolfeboro, NH
6-10 August 1984

First International Conference on the
Structure of Surfaces (ICSOS)
Dr. Gabor Somorjai
Lawrence Berkeley Laboratory
Berkeley, CA
13-16 August 1984

1984 Gordon Research Conference in Organometallic Chemistry
Dr. J. W. Faller
University of Rhode Island
Proctor Academy
Andover, NH
13-17 August 1984

1984 Gordon Research Conference on Vibrational Spectroscopy
Dr. Cherry Murray
University of Rhode Island
Brewster Academy
Wolfeboro, NH
20-24 August 1984

ACTIVE RESEARCH EFFORTS

As of 30 September 1984

Alphabetical by Principal Investigator

CHEMICAL TECHNIQUES - DENTON W. ELLIOTT

Surface Processes and Trace Analysis Using Solid Electrodes AFOSR-83-0004	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, NY 14214
Evaluation of Chemical and Atmospheric Sciences Research F49620-84-C-0073	Joseph E. Earley Department of Chemistry Georgetown University Washington, DC 20057
New Materials for Electrochemical Cells AFOSR-83-0052	John B. Goodenough Peter G. Dickens Inorganic Chemistry Laboratory Oxford University Oxford, UK OX1 3QR
Synthesis Structure and Reactivity of Molecules Attached to Electrode Surfaces AFOSR-81-0149	Arthur T. Hubbard Department of Chemistry University of California, Santa Barbara Santa Barbara, CA 93106
Ambient Temperature Chloraluminate Ionic Liquids AFOSR-84-0292	Robert A. Osteryoung Janet Osteryoung Department of Chemistry State University of New York Buffalo, NY 14214
Fast Protonic Conducting Solid Electrolytes AFOSR-82-0221	Mark A. Ratner Donald H. Whitmore Department of Chemistry Northwestern University Evanston, IL 60201
Chromatographic and Mass Spectrographic Separation and Analysis AFOSR-84-0093	Robert E. Sievers Department of Chemistry University of Colorado Boulder, CO 80309

Molecular Structural Basis of
Electrode Kinetics
AFOSR-83-0011

Michael Weaver
Department of Chemistry
Purdue University
West Lafayette, IN 47907

Analytical Gas Phase
Spectrometry and Combustion
Diagnostics
F49620-84-C-0002

James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, FL 32611

SURFACE CHEMISTRY - CAPTAIN LEE E. MYERS

Reactions of Organic Molecules on Metal Surfaces AFOSR-82-0302	Jay B. Benziger Department of Chemical Engineering Princeton University Princeton, NJ 08544
Reevaluation of Surface Electronic Properties of Barium Oxide AFOSR-84-0129	Joseph Cunningham Department of Chemistry University College, Cork Cork, IE
Investigation of Surface Phenomena in Termionic Energy Conversion AFOSR-83-0105	Paul R. Davis Lynwood W. Swanson Dept of Appl Phy & Elec Engrg Oregon Graduate Center Beaverton, OR 97006
Modulated Molecular Beam Investigation of the Reactions of Fluorine and Oxygen with Silicon Surfaces AFOSR-83-0115	Thomas Engel Department of Chemistry University of Washington Seattle, WA 98195
High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium AFOSR-83-0131	James L. Erskine John M. White Department of Physics University of Texas Austin, TX 78712
Theoretical Studies of Laser-Induced Molecular Rate Processes: Topics in Line Broadening and Spectroscopy AFOSR-82-0046	Thomas F. George Department of Chemistry University of Rochester Rochester, NY 14627
Measurement of Rate Constants of Elementary Gas Reactions of Importance to Upper Atmosphere and Combustion Systems AFOSR-80-0207	Frederick Kaufman Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260
Electronic Energy Transfer Processes in the Akali/Akaline Earth Metal Vapors AFOSR-84-0272	Stephen R. Leone Alan C. Gallagher Department of Chemistry University of Colorado Boulder, CO 80309
Threshold Electron Studies of Gas-Surface Interactions AFOSR-83-0260	P. Terrence Murray University of Dayton Research Institute 300 College Park Avenue Dayton, OH 45469

Theoretical Investigation of Homogeneous and Heterogeneous Reactions in the Chemical Vapor Deposition of Silicon from Silane AFOSR-82-0311	Lionel M. Raff Department of Chemistry Oklahoma State University Stillwater, OK 74078
Dynamics of Gas-Surface Interactions AFOSR-84-0073	Steven J. Sibener Department of Chemistry University of Chicago Chicago, IL 60637
Surface Generation of Electronically Excited States of O_2 F49620-82-K-0025	T. G. Slanger Molecular Physics Laboratory SRI International 333 Ravenswood Avenue Menlo Park, CA 94025
Program to Explore and Evaluate the Influence of Surface Structural Defects on the Chemical Properties of Solid Surfaces AFOSR-83-0302	Peter C. Stair Department of Chemistry Northwestern University Evanston, IL 60201
Investigation of Coulped Surface and Bulk Reaction Phenomena Using CEAPS AFOSR-84-0301	Bruce J. Tatarchuk Department of Chemical Engrg Auburn University Auburn, AL 36849
Secondary Ion Mass Spectrometry Studies of Solids and Surfaces AFOSR-82-0057	Nicholas Winograd Department of Chemistry Pennsylvania State University University Park, PA 16802
Chemistry of Non-Equilibrium Film Deposition F49620-81-C-0074	Francis J. Wodarczyk Rockwell International Science Center Thousand Oaks, CA 91360
Structure of Molecular Adsorbates on Surfaces AFOSR-82-0133	John T. Yates, Jr. Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260

CHEMICAL STRUCTURES - DR. DONALD R. ULRICH

Microdesigning of Lightweight/ High Strength Ceramic Materials AFOSR-83-0375	Ilhan A. Aksay Dept of Mining Metallurgical University of Washington Seattle, WA 98195
Large Molecule Diffusion and Interfacial Effects in Oriented Polymers AFOSR-82-0290	R. Edward Barker, Jr. Kenneth R. Lawless Department of Materials Science University of Virginia Charlottesville, VA 22901
Light Scattering Studies of Molecular Dynamics in Molecular Crystals, Liquid Crystals, and Polymers for Applications in Chemical Defense AFOSR-82-0122	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, CO 80521
Basic Research on Processing of Ceramics for Space Structures F49620-84-C-0097	H. K. Bowen Materials Processing Massachusetts Institute of Technology Cambridge, MA 02139
New Organic and Organometallic Materials with Non-Linear Optical Properties for Optical Signal Processing AFOSR-84-0363	Dwaine O. Cowan Dean W. Robinson Department of Chemistry Johns Hopkins University Baltimore, MD 21218
Pulsed Microwave Characterization of Conducting Polymers AFOSR-82-0184	Larry R. Dalton Department of Chemistry University of Southern California Los Angeles, CA 90007
Physical and Morphological Properties of Polymers AFOSR-82-0009	Paul J. Flory Department of Chemistry Stanford University Stanford, CA 94305
Structure and Refinement of Ordered Aromatic Heterocyclic Polymers by Diffraction Methods: Application of Results to Electro-Optics Phenomena AFOSR-84-0364	Albert Fratini Department of Chemistry University of Dayton Dayton, OH 45469

Fluoride Glasses For Bulk Optical and Waveguide Applications F49620-84-C-0098	John R. Gannon Corning Glass Works Exploratory Research Department Corning, NY 14831
Molecular Optics: Nonlinear Optical Processes in Organic and Polymeric Chrystals and Films AFOSR-84-0135	A. F. Garito Department of Physics University of Pennsylvania Philadelphia, PA 19104
Improvement and Optimization of Internal Damping in Fiber Reinforced Composite Materials AFOSR-83-0156	Ronald F. Gibson Dept of Mechanical Engineering Univ of Idaho Moscow, ID 83843
Microstructural Engineering of Lightweight Ceramics Structures F49620-83-C-0078	David Green Dept of Engineering Rockwell International Thousand Oaks, CA 91360
Novel Liquid Crystals - Polymers and Monomers - As Nonlinear Optical Materials AFOSR-84-0249	Anselm C. Griffin Dept of Chemistry and Polymer Science University of Southern Mississippi Hattiesburg, MS 39406
Ultrastructure Processing Research on Advanced Ceramics and Composites F49620-83-C-0072	Larry L. Hench Department of Materials Science University of Florida Gainesville, FL 32611
NMR Study of Disordered Materials under Extreme Conditions of Pressure and Temperature AFOSR-81-0010	Jiri Jonas Department of Chemistry University of Illinois Urbana, IL 61801
Ultrastructure Processing and Characterization of Polymers F49620-83-K-00006	Frank E. Karasz Polymer Science & Engineering University of Massachusetts Amherst, MA 01003
Improved Structural Polymers Alloys and Composites F49620-84-C-0051	Frank E. Karasz Polymer Science & Engineering University of Massachusetts Amherst, MA 01003
Fundamental Studies of Time-Dependent Response and Fracture of Cross-Linked Polymers F49620-83-C-0032	Frank N. Kelley Maurice Morton Institute of Polymer Science University of Akron Akron, OH 44325

Preparation & Properties of Halide Glasses and Glass-Polymer Composites AFOSR-84-0022	John D. Mackenzie Dept of Mat Science & Engrg School of Engrg & Applied Sc University of California Los Angeles, CA 90024
New Materials for Spacecraft Stability and Damping - A Feasibility Study AFOSR-83-0221	John D. Mackenzie Dept of Mat Science & Engrg School of Engrg & Applied Sc University of California Los Angeles, CA 90024
High-Performance Polymeric Materials AFOSR-83-0027	James E. Mark Department of Chemistry University of Cincinnati Cincinnati, OH 45221
PBT, PBO-Based Hybrid Polymeric Materials with Nonlinear Optical Properties or High Electrical Conductivity AFOSR-84-0354	Tobin J. Marks Stephen H. Carr Department of Chemistry Northwestern University Evanston, IL 60201
Research to Identify and Monitor Emerging Technologies F49620-84-C-0099	Patrick P. McDermott B & K Dynamics, Inc. 3204 Monroe Street Rockville, MD 20850
Aromatic Polyester-Polysiloxane Block Copolymers: Multiphase Transparent Damping Materials AFOSR-83-0201	James E. McGrath Department of Chemistry Virginia Polytechnic Institute and State University 301 Burruss Hall Blacksburg, VA 24061
Ultra Low Thermal Expansion Ceramics AFOSR-83-0291	H. A. McKinstry Pennsylvania State University Materials Research Laboratory Philadelphia, PA 16802
Surface Chemistry and Structural Effects in the Stress Corrosion of Glass and Ceramic Materials AFOSR-82-0013	Carlo G. Pantano Department of Materials Pennsylvania State University University Park, PA 16802
Molecular Mechanics of Polymeric Interactions in Relation to Chemical Defense AFOSR-82-0118	Paras N. Prasad Department of Chemistry State University of New York Buffalo, NY 14260
Development of Spacecraft Materials and Structures Fundamentals F49620-83-C-0101	Svante Prochazka Stephen L. Dole Ceramics Div., Inorganic Mat Lab General Electric Co Schenectady, NY 12301

Ion-Exchanged Waveguides for Signal Processing Applications - A Novel Electrolytic Process AFOSR-84-0369	V. Ramaswamy Department of Electrical Engineering University of Florida Gainesville, FL 32611
Exploitation of the Sol-Gel Process in Preparation of New Ceramics AFOSR-83-0212	Rustum Roy Materials Research Laboratory Pennsylvania State University University Park, PA 16802
Investigation of Non-Linear Optical Behavior of Semiconductor for Optical Switching AFOSR-84-0395	Joseph H. Simmons Department of Materials Science and Engineering University of Florida Gainsville, FL 32611
Organooptics: Nonlinear Optical Properties of Polymers F49620-84-C-0110	Dagaobert E. Stuetz Celanese Research Company 86 Morris Avenue Summitt, NJ 07901
Improvement and Optimization of Internal Damping in Fiber Reinforced Composite Materials AFOSR-83-0154	C. T. Sun Dept of Engineering Sciences University of Florida Gainesville, FL 32611
Microstructure of Amorphous and Semi-Crystalline Polymers AFOSR-81-0011	Donald R. Uhlmann J. B. Vander Sande Department of Materials Science & Engineering Massachusetts Institute of Technology Cambridge, MA 02139
Ordered Polymers for Space Applications F49620-83-K-0036	James F. Wolfe David B. Cotts Polymer Sciences Dept SRI International Menlo Park, CA 94025

MOLECULAR DYNAMICS - CAPTAIN LEE E. MYERS

Kinetics of Intra and Inter Excitation Energy Transfers F49620-84-C-0031	Simon H. Bauer Department of Chemistry Cornell University Ithaca, NY 14853
Energy Disposal in Ion-Molecule Reactions AFOSR-82-0035	Michael T. Bowers Department of Chemistry University of California Santa Barbara, CA 93106
Study in Molecular Lasers AFOSR-84-0127	George Burns Department of Chemistry University of Toronto Toronto, Ontario, Canada M5S 1A1
Physical Chemistry of Energetic Nitrides AFOSR-84-0031	R. D. Coombe Department of Chemistry University of Denver Denver, CO 80208
Group IIA Metastable Collision Complexes: Spectroscopy and Behavior in Intense Radiation Fields AFOSR-84-0027	John Cooper Keith Burnett Department of Physics and Institute for Lab Astrophysics University of Colorado Boulder, CO 80309
Ion Photofragment Spectroscopy: Structure and Dissociation of Molecular Ion F49620-81-K-0006	Philip C. Cosby James R. Peterson Molecular Physics Laboratory SRI International Menlo Park, CA 94025
Vibrational Relaxation Rates and Pathways in Highly Excited Molecules AFOSR-82-0244	F. Fleming Crim Department of Chemistry University of Wisconsin Madison, WI 53706
Gas-Phase Photoelectron Spectroscopy of Metals and Metal Oxides of Importance in the Upper Atmosphere AFOSR-83-0283	John M. Dyke Department of Chemistry The University of Southampton Highfield Southampton, SO9 5NH, UK
Rotational and Vibrational Spectra of Molecular Clusters F49620-83-C-0007	Thomas R. Dyke Department of Chemistry University of Oregon Eugene, OR 97403

Molecular Collision Processes In Gases and at Surfaces F49620-84-C-0038	John B. Fenn S. Ryali Department of Engineering and Applied Science Yale University New Haven, CT 06520
Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties F49620-83-C-0010	Robert W. Field James L. Kinsey Department of Chemistry, Rm 6-223 Massachusetts Institute of Technology Cambridge, MA 02139
Spectroscopic Studies of the Products of the Reactions of Electronically Excited Atoms and Small Molecules AFOSR-83-0188	Michael F. Golde Chemistry Department Univ of Pittsburgh Pittsburgh, PA 15260
Laser-Induced Kinetics: An Experimental and Theoretical Program for the Study of Elementary Chemical Processes F49620-83-K-0001	David M. Golden Michel J. Rossi Physical Sciences Division SRI International Menlo Park, CA 94025
Study of Molecular Sources of Ionospheric Holes AFOSR-84-0109	Steven L. Guberman Smithsonian Institution 60 Garden Street Cambridge, MA 02138
Spectroscopy and Energy Transfer Kinetics of Excited State of the Interhalogens: Laser Induced Fluorescence Studies of Metastable States AFOSR-83-0173	Michael Heaven Department of Chemistry Illinois Institute of Technology Chicago, IL 60616
Rotational Relaxation Studies of Hydrogen Fluoride F49620-83-C-0098	John J. Hinchen United Technologies Research Center Energy Research Laboratory East Hartford, CT 06108
Laser Studies of Halogens and Oxygens F49620-83-K-0012	Paul L. Houston Department of Chemistry Cornell University Ithaca, NY 14853
Theoretical and Experimental Studies in Reactive Scattering AFOSR-82-0341	Aron Kuppermann Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, CA 91125

State-Resolved Dynamics of Ion-Molecule Reactions in a Flowing Afterglow F49620-83-C-0013	Stephen R. Leone G. Barney Ellison Veronica M. Bierbaum Department of Chemistry University of Colorado Boulder, CO 80309
Analysis and Prediction of Experimental Results for Elementary Molecular Processes AFOSR-81-0030	Raphael D. Levine James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Study of Singlet Oxygen - Pentavalent Phosphorus Reactions F49620-82-C-0045	Leonard J. Marabella Chemical Physics Department TRW Incorporated Redondo Beach, CA 90278
Energetic and Collision Dynamics of Electronic Transition Laser Systems F49620-81-C-0097	H. Michels Robert H. Hobbs United Technologies Research Center East Hartford, CT 06108
Nanosecond IR Spectroscopy and Vibrational Enhancement of Chemical Reactions AFOSR-82-0031	George Pimentel Department of Chemistry University of California at Berkeley Berkeley, CA 94720
The Molecular Dynamics of Reactions Forming Electronically Excited Products AFOSR-81-0027	John C. Polanyi Department of Chemistry University of Toronto Toronto, Ontario, Canada M5S 1A1
Theoretical Methods for Chemical Kinetics AFOSR-84-0106	Herschel Rabitz Chemistry Department Princeton University Princeton, NJ 08544
Experimental and Theoretical Studies of Molecular Dynamics F49620-83-C-0002	Stuart A. Rice Department of Chemistry University of Chicago Chicago, IL 60637
Theory and Experiments on Chemical Instabilities F49620-84-C-0030	John Ross Department of Chemistry Stanford University Stanford, CA 94305
Reactions of Laser-Generated Free Radicals at Semi-Conductor Surfaces AFOSR-83-0007	Jeffrey I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139

Spectroscopic Studies of the Halogens
AFOSR-83-0110

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Dynamics of Fragmentation of Electronically Energetic Species Produced by Short-Pulsed UV Excitation of Molecules In the Gas Phase AFOSR-84-0019

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Studies of Energy Storage and Transfer in Gas Lasers
AFOSR-82-0037

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Laser Kinetic Spectroscopy of Unimolecular and Bimolecular Processes in the Gas Phase
AFOSR-83-0022

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State Identification of Reaction Products
F49620-82-C-0033

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CHEMICAL REACTIVITY AND SYNTHESIS - DR. ANTHONY J. MATUSZKO

New Inorganic-Organic High Polymer Systems AFOSR-84-0147	Dr. Harry R. Allcock Department of Chemistry Pennsylvania State University 152 Davey Laboratory University Park, PA 16802
Distibines, New One-Dimensional Materials AFOSR-81-0099	Arthur J. Ashe, III Department of Chemistry University of Michigan Ann Arbor, MI 48109
Synthesis and Chemistry of Polynitroalkanes and Polynitroolefins F49620-83-K-0028	Clifford D. Bedford Robert J. Schmitt Chemistry Laboratory SRI International Menlo Park, CA 94025
New Approaches to the Synthesis of Novel Organosilanes AFOSR-84-0008	Philip Boudjouk Department of Chemistry North Dakota State University Fargo, ND 58105
New Approaches to Functionalized Fluorocarbons AFOSR-80-0259	Donald J. Burton Department of Chemistry University of Iowa Iowa City, IA 52242
A New Approach to Highly Fluorinated Lubricants AFOSR-82-0084	R. D. Chambers Department of Chemistry University of Durham Durham, England DH1 3LE
Development of Practical MO Techniques for the Prediction of Properties and Behavior of Materials F49620-83-C-0024	Michael J. S. Dewar Department of Chemistry University of Texas Austin, TX 78712
Picosecond Laser Studies of Chemical Intermediates AFOSR-84-0013	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, NY 10027
Quantum-Chemical Studies of Enzyme Inhibitors and Related Compounds AFOSR-82-0100	Carl S. Ewig John R. Van Wazer Wolf D. Dettbarn Department of Chemistry Vanderbilt University Nashville, TN 37235

Electrolytic Preparation of Novel Azidodinitro Compounds
F49620-83-C-0036

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Ground and Excited State Reactions of Phosphonofluoridic Acids and Esters and Their Isomers
AFOSR-82-0190

Control of the Urethane Cure Reaction with Solid, Blocked Isocyanates
F49620-84-C-0059

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Effect of Toluene on the Solubility of Biohazardous Volatile Synthetic Organic Compounds
AFOSR-83-0175

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Polysilylated Unsaturated Molecules
AFOSR-83-0244

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Novel Diaklyamino Derivatives of Phosphorus and Silicon
AFOSR-84-0050

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New Experimental Flourine Chemistry: New Experimental Challenges in Elemental Fluorine Chemistry AFOSR-82-0197

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Structure and Reactivity of Per-fluorinated Annulenes and Their Relatives
AFOSR-83-0047

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Investigation of Deviations from Ideality in the Two Liquid Phase Region of Systems of Medium Molecular Weight Hydrocarbon Mixtures and Water
AFOSR-83-0036

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Synthesis of New Polynitro-polyhedranes
AFOSR-84-0085

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Fabricable Polymers for Use Under Extreme Conditions AFOSR-82-0007	Carl S. Marvel Department of Chemistry University of Arizona Tucson, AZ 85721
Structure and Properties of Novel Compounds of Silicon Germanium, and Tin AFOSR-84-0065	Josef Michl Department of Chemistry University of Utah Salt Lake City, UT 84112
Synthesis of Novel Nitrogen and Phosphorus Heterocycles F49620-82-C-0021	Kay L. Paciorek Chemical & Materials Research Ultrasystems, Inc. Irvine, CA 92664
The Chemistry of Precursors to Silicon-Carbide AFOSR-83-0209	Morey A. Ring H. Edward O'Neal Department of Chemistry San Diego State University San Diego, CA 92182
Basic Research in Novel Inorganic Reagents and Fluorocarbon Chemistry F49620-81-C-0020	C. J. Schack Rocketdyne Division Rockwell International Canoga Park, CA 91304
Organosilicon Compounds and Organosilicon Polymer Intermediates AFOSR-83-0003	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Synthesis of Difluoraminoxy, Difluoramino or Fluorodiazonium Containing Materials AFOSR-82-0247	Jean'ne M. Shreeve Department of Chemistry University of Idaho Moscow, ID 83843
Properties of Reactive Species Generated at High Temperatures and Their Low Temperature Reactions to Form Novel Substances AFOSR-82-0195	Philip S. Skell Department of Chemistry Pennsylvania State University University Park, PA 16802
Compounds Containing Hetero-nuclear Metal-Metal Bonds AFOSR-82-0070	F. G. A. Stone Department of Inorganic Chemistry University of Bristol Bristol, BS8 1TS, UK
Theoretical Study of Penta-valent Phosphorus AFOSR-82-0114	Andrew Streitwieser, Jr. Department of Chemistry University of California Berkeley, CA 94720

Synthesis and Chemistry of
Energetic Metallotetraazadienes
AFOSR-83-0021

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Structural and Dynamics Studies
of Materials Possessing High
Energy Content
AFOSR-84-0040

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Chemistry of New Silicon Con-
taining Polymers and Triply Bonded
Silicon Intermediates
AFOSR-82-0333

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Chemical Reactions and Properties
of Organosilicon Compounds
Related to New Materials
F49620-83-C-0044

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ATMOSPHERIC SCIENCES
LT COL GERALD J. DITTBERNER
LT COL TED S. CRESS
MAJOR JAMES I. METCALF (USAF Reserve)

Measurement of Horizontal Structures and Wavelengths (5-500KM) in Mesospheric Gravity Waves, Tides and Winds Workshop and Design Study
AFOSR-84-0121

Gene W. Adams
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Magnetosphere - Ionosphere - Thermosphere, Radar Studies Using Three High-Latitude Incoherent - Scatter Stations
F49620-83-K-0005

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Behavior of the Atmosphere in the Desert Planetary Boundary Layer
AFOSR-84-0036

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The Growth Potential of Corona Discharges From Aircraft Flying In Precipitation
AFOSR-83-0083

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Analysis and Prediction of Mid-Lattitude Mesoscale Convective Precipitation Systems
AFOSR-83-0064

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Nonlinear Internal Gravity-Wave Propagation, Saturation, and Absorption in the Atmosphere
F49620-83-C-0061

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Analyze Frontal-Passage Data From the Sousy-VHF-Radar
AFOSR-83-0100

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Dynamical-Chemical Coupling in the Mesosphere and Lower Thermosphere
AFOSR-84-0182

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Studies of the Auroral Zone Ionosphere Using the MITHRAS Data Base AFOSR-83-0002	John C. Foster Massachusetts Inst. of Tech. Haystack Observatory Westford, MA 01886
Theoretical and Observational Studies of Gravity Wave Saturation Processes AFOSR-82-0125	David Fritts Geophysical Institute University of Alaska Fairbanks, AK 99701
The Turbulent Gravity Wave-Critical Level Encounter in the Evolution of Atmospheric Flow F49620-84-C-0048	John R. Grant Gould Defense System, Inc. 11 Technology Plaza Aquidneck Industrial Park Middletown, RI 02840
Atmospheric Structure Variations AFOSR-84-0045	Gerald V. Groves Dept of Physics & Astronomy University College London Gower Street London, WCIE 6BT England
A Theoretical Framework for Examining Geographical Variability in the Microphysical Mechanisms of Precipitation Development AFOSR-82-0179	David B. Johnson Illinois State Water Survey P.O. Box 5050, Station A Champaign, IL 61820
The Morphology of Broken Cloud Fields over Ocean and Land Surfaces AFOSR-84-0357	Joachim H. Joseph Department of Geophysics and Planetary Sciences Tel-Aviv University Tel-Aviv, Israel 69978
Construction of University of Missouri-Rolla's Full Scale Cloud Simulation Chamber F49620-80-C-0090	James J. Kassner, Jr. D. R. White Department of Physics University of Missouri-Rolla Rolla, MO 65401
The Stability of Atmospheric Fields Induced By Localized Topography and Heat Sources AFOSR-83-0069	Lee-Or Merkine Department of Mathematics Technion-Israel Institute of Tech Haifa, Israel

Synoptic-Scale Vertical Wind and Mesoscale Horizontal Wind Variability from MST Radar Observations F49620-82-C-0029	G. Nastrom Department of Meteorology Control Data Corporation Minneapolis, MN 55440
Measurement of Atmospheric Transmission over Long Path in the Infrared Spectral Region AFOSR-83-0023	Uri P. Oppenheim S. Lipsom Department of Physics Technion-Israel Inst of Tech Haifa, Israel
Partial Support of Board on Atmospheric Sciences and Climate AFOSR-84-0062	John Perry National Acadamy of Sciences Washington DC 20418
Effects of Mountain Ranges on Mesoscale Systems Development AFOSR-82-0162	Elmar Reiter Teizi Henmi Department of Atmospheric Sciences Fort Collins, CO 80523
Comparison of Ionospheric Model Predictions With MITHRAS Observations AFOSR-84-0029	R. W. Schunk Center for Atmospheric and Space Sciences Utah State University Logan, UT 84322
Infrared Airglow Clutter F49620-83-C-0122	James C. Ulwick Utah State University Space Dynamics University Logan, UT 84322
Committee on Solar-Terrestrial Research AFOSR-84-0028	Thomas M. Usselman National Acacemy of Sciences Washington, DC 20418
High-Latitude Ionospheric Irregularities F49620-83-K-0025	James F. Vickrey Radio Physics Laboratory SRI International Menlo Park, CA 94025

CHEMICAL TECHNIQUES

The Chemical Techniques program encompasses research in the traditional chemical sub-disciplines of analytical chemistry and electrochemistry.

The emphasis in the electrochemistry area was on an understanding of electrochemical systems that may ultimately be related to electrical power generation and storage. This includes a fundamental understanding of processes occuring at electrode surfaces and also the study of non-traditional electrolytes. The nature of electrode processes was approached from several directions. The adsorption or deposition of monolayers on electrodes were detected and characterized by observing directly the mass of the layers with the quartz crystal electrode surfaces. Electrochemical kinetics and its relation to molecular structure was also a topic of interest.

Non-traditional electrolytes included molten salts and solid electrolytes. The chemical and electrochemical characterization of novel molten salts that are liquid at and below room temperature is an area of great potential and growing activity. Solid electrolytes that display fast ion conduction are of interest from synthetic and mechanistic viewpoints.

The field of analytical chemistry was limited to two areas concerned with detection. The detection and diagnosis of plasma and normal chemical flames is important for fundamental reasons and also reveals new analytical techniques. The chromatographic separation and mass spectrographic analysis of environmental samples is an important analytical problem.

SURFACE CHEMISTRY

FY 84 saw the culmination of a four year effort to redirect and significantly expand the surface chemistry program at AFOSR. In 1981, the surface chemistry program consisted of seven projects concentrated in the applied fields of adhesion and lubrication. At the close of FY84, the surface chemistry program had grown to include 16 active research projects. Of the original seven projects only one remained. During this period the research interests changed from adhesion and lubrication to fundamental molecular level studies of surface reactions and thin films. These research areas shared nearly equally in the investment with 55% invested in surface reactions and 45% in thin films. During FY 84, the program experienced reasonable growth with the addition of two new principal investigators, Drs. S. Sibener, University of Chicago and B. Tatarchuk, Auburn University. In addition to the annual Contractors' Conference, three scientific conferences were supported: Applied Surface Science, the International Conference on the Structure of Surfaces, and Catalytic Reaction Mechanism: The Role of Surface Structure and Composition (MRS).

FY 85 will be the beginning of a period of change due to changes in management personnel. Although the FY 85 investment profile will be set well before any personnel changes occur, the conceptualization of new research thrusts will begin by the end of the year.

The final topic this year is the success of our annual Molecular Dynamics and Surface Chemistry Contractors' Conference. This meeting was held at the Air Force Weapons Laboratory, Kirtland AFB, Albuquerque, NM. It was a two and one-half day meeting with speakers and participants from both the surface chemistry and molecular dynamics programs. Several changes were made compared to previous meeting formats. Several general topic or survey speakers were invited from among presently supported researchers and Air Force scientists. In addition, a book of abstracts of both speakers and non-speakers was compiled and printed before the meeting and published with corrections after the meeting. Both of these changes were suggested by participants of previous meetings.

CHEMICAL STRUCTURES

During FY 84 a major initiation in the area of Chemical Structures was undertaken in nonlinear optical polymers, organics and sol gels for optical signal processing. Electrooptical polymer research focuses on liquid crystalline polymers. Early results show that these have exceptionally large, purely electronic $\chi^{(3)}$ and therefore ultrafast switching (10^{-14} to 10^{-15} seconds) with lossless virtual optical excitation at low energies ($1x10^{-12}$ joule at 10^{12}Hz). This remains an area of high interest for investment. The investigators on this initiative are as follows:

ELECTROOPTIC POLYMERS

Organooptics: Nonlinear Optical Properties of Polymers, Dr. Allen Buckley, Celanese Research Company.

Structural and Refinement of Ordered Aromatic Heterocyclic Polymers by Diffraction Methods: Application of Results to Electrooptics Phenomena, Albert Fratini, University of Dayton.

Molecular Optics: Nonliner Optical Processes in Organic Crystals and Fibers, Anthony F. Garito, University of Pennsylvania

Novel Liquid Crystals - Polymers and Monomers - As Nonlinear Optical Materials, Anselm C. Griffin, University of Southern Mississippi.

PBT, PBO - Based Hybrid Polymeric Materials with Nonlinear Optical Properties and High Electrical Conductivity, Tobin J. Marks and Stephen H. Carr, Northwestern University.

Molecular Mechanics of Polymeric NLO Reactions, Paras N. Prasad, SUNY, Buffalo.

Nonlinear Optical Polymers, Gary E. Wnek, Massachusetts Institute of Technology.

Electrooptic Polymers, Dagobert E. Stuetz, Celanese Research Company.

ORGANICS AND ORGANOMETALLICS

New Organic and Organometallic Materials with Nonlinear Optical Properties, Dwaine O. Cowan and Dean W. Robinson, Johns Hopkins University.

Design, Synthesis and Study of New Electro-Optical Molecular Solids, Theodore O. Poehler and Richard S. Potember, Johns Hopkins Applied Physics Laboratory.

SOL-GELS

Ion-Exchanged Waveguides for Signal Processing Applications - A Novel Electrolytic Process, V. Ramaswamy, University of Florida.

Microdesigning of Sol Gels and Nonlinear Optical Semiconductor Structures, Joseph H. Simmons, University of Florida.

Sol Gels for Electrooptics, John D. Mackenzie, University of California, Los Angeles

MOLECULAR DYNAMICS

Throughout FY1984 the Molecular Dynamics program remained under the direction of the manager of the Surface Chemistry program, Captain Lee E. Myers, while a search was made for a permanent civilian program manager. Under Capt Myers' experienced guidance the program continued to prosper, in part because of an infusion of funds to enhance the Chemical Laser effort. During FY84 two Gordon Conferences, one on Vibrational Spectroscopy and one on Electron Spectroscopy, were supported from Molecular Dynamics Task funds, as was an International Conference on Radiationless Transitions.

The current AFOSR Molecular Dynamics program is keyed primarily to two general areas of interest, reflecting the interests of the Air Force Laboratories with which we most frequently interact. Chemical laser-related research is coupled closely with activities and interests at the Air Force Weapons Laboratory in Albuquerque, NM, while efforts related to atmospheric chemistry are of interest to research at the Air Force Geophysics Laboratory near Boston.

Research on chemical lasers and related spectroscopy and kinetics dominated the FY84 Molecular Dynamics budget by taking a 44% share. Although Air Force interests in new chemical laser concepts remains strong, the current level of AF-funded basic research in this area is expected to drop slightly in the near term. Work units related to atmospheric chemistry, dealing mostly with ion-molecule reactions of atmospheric species, had the next largest share of the Task budget at 24%. Interactive Dynamics, an area concerned with energy flow in reacting systems, accounted for 22% of the Task budget, and a slightly increasing proportion of new work is expected to be funded in this area. Research on energetic materials, concerned with thermal decomposition of fuels, explosives, and propellants, took a relatively small 9% share of Molecular Dynamics funds.

CHEMICAL REACTIVITY AND SYTHESIS

In this year's review of Chemical Reactivity and Synthesis we will give you a brief account of our ongoing program together with an indication of where we might consider proposals for new work.

For more than 20 years our biggest program in the Chemical Reactivity and Synthesis area has been in the new chemistry and new discoveries of organometallics. The emphasis has been on the fundamental chemistry of organosilicon compounds and their derivatives. The basic knowledge acquired has made a significant contribution to better understanding organosilicon chemistry. It has also been quite useful in the synthesis of polymeric silanes as precursors for high temperature, high strength ceramics. The unique properties of organosilanes has made them promising candidates as photoresist materials, "living polymer" catalysts, and environment resistant hydraulic fluids. Because of our rapid expansion in this area of research over the past five years and our funding limitations, any additions of new work to this program will have to be comprised of new ideas or novel concepts. Within these same monetary restrictions, we have an interest in exploring the chemistry of new metallic and intermetallic organometallics and learning more about Ti, Zr, Hf and Ta organometallics.

A second area of focus over the past few years has been inorganic and organic fluorine chemistry. Our program in this area has leveled off and has decreased somewhat from what it was 10 years ago. The emphasis has been on new approaches to making fluorocarbon ethers and fluorocarbon polymers, phosphatriazines with fluorocarbon ether side groups, and functionalization of fluorocarbon compounds. Here once again any new ideas will be welcome.

In FY82 we had no program in Energetic Materials (the synthesis and reactivity of high energy propellant and explosive ingredients). With encouragement from Len Caveny of AFOSR's Aerospace Sciences Directorate, Frank Roberto and others at the Rocket Propulsion Laboratory (Edwards AFB), and Dick Miller of ONR, we started up a propellants and explosives synthesis program in FY83 which at the present time is running at close to a million dollars a year. There was a considerable amount of thought and planning put into this program before we decided to go ahead with it. Still in its infancy, the program has been extremely productive resulting in a lot of new chemistry. Some of the new compounds synthesized will be tested in propellant formulations. At present we are limited in funding, but we are always open to exciting new ideas. Most of the research efforts we currently have in the program are funded for three years each. Proposals for further funding will be in competition with completely new proposed research efforts.

About 20 to as much as 30% of the program in Chemical Reactivity and Synthesis is devoted to research covering a broader area than the focused programs I have described. Included are new concepts which rank high for their scientific importance but may seem to be low on relevance. We will listen to any new ideas which have a sound scientific basis.

ATMOSPHERIC SCIENCES

As the single manager of Air Force basic research, AFOSR supports an extramural atmospheric research program and an in-house research program at Air Force Laboratories. The in-house and contractual basic research at Air Force Geophysics Laboratory (AFGL) dominates the overall atmospheric science basic research program and is oriented toward the support of exploratory development efforts in the laboratory. The extramural program sponsored directly by AFOSR is of wider scope and higher risk, as it seeks to produce the fundamental knowledge that will support problem-solving efforts in the future. Close coordination between AFOSR and AFGL insures that the respective efforts are complementary.

The purpose of the AFOSR atmospheric sciences basic research program is to stimulate and support innovative research that will ultimately lead to a more thorough understanding of the fundamental physical processes of the atmosphere. The scope of the program includes phenomena at scales from molecular to global and from the earth's surface to the outer limits of the atmosphere. This domain includes nearly all of the geophysical processes influencing the design and performance of current and proposed Air Force systems, including space-based communications and surveillance systems. Environmental effects on space-based systems, e.g., drag, electrostatic charging, and surface chemistry, are generally addressed in other AFOSR program areas. Magnetospheric processes are included in this program only to the extent that they affect the behavior of the ionosphere.

The atmospheric sciences program comprises two traditional research areas: tropospheric meteorology and the upper atmosphere (including the ionosphere). In each of these areas most of the funding is concentrated in a few topics of special emphasis. This approach to the allocation of funds, together with our encouragement of collaborative efforts among principal investigators, is intended to maximize the likelihood of major advances in the selected areas. In FY84 the meteorology program continued to emphasize mesoscale processes, cloud physics, and atmospheric dynamics, while the upper atmosphere program emphasized a large cooperative analytical effort aimed at understanding the global character of auroral zone variability.

Research in mesoscale meteorology is aimed at the development of improved models for predicting atmospheric phenomena. The present uncertainties of such predictions are due, at least in part, to the imperfect representation of such processes as convection, radiation, and the exchange of heat and moisture with the earth's surface through the planetary boundary layer. Significant progress has been made at Colorado State University both in the measurement of exchange processes at the surface and in the representation of these processes in a mesoscale model. Scientists at the Pennsylvania State University have investigated the roles of surface wind divergence, moisture distribution, and vertical temperature structure on the development of mesoscale convective complexes. Research in mesoscale meteorology sponsored by AFOSR is expected to support the objectives of the National Stormscale Operational and Research Meteorology (STORM) Program in the years ahead.

Efforts in cloud physics include water drop nucleation, precipitation development in clouds, optical and infrared scattering and transmission in

clouds, and electrification. Closely related areas of interest include aerosol physics and the effects of aerosols and water vapor on optical and infrared signal propagation. The two cloud simulation chambers were completed at the University of Missouri and are now being used in studies of cloud initiation and growth.

Research in atmospheric dynamics encompasses the planetary boundary layer, the transport of momentum and energy by gravity waves, and the dynamics of synoptic-scale weather systems. Progress in the latter two areas has been greatly facilitated by the use of high-power VHF and UHF radars for measurement of vertical profiles of horizontal and vertical air motion with high resolution in time. As these radars are also capable of wind measurements on the stratosphere and mesosphere, they continue to be a key part of several AFOSR programs.

The primary emphases of the upper atmospheric research program are the temporal and spatial morphology of ionospheric structure, particularly electron density irregularities and gradients, and the dynamics of the upper atmosphere. The issues involved in this research are global in character and include auroral zone phenomenology, equatorial F-region irregularities, dynamics of the neutral components, distribution of chemical species, solar influences on the neutral atmosphere, ionospheric disturbances, deliberate and inadvertent ionospheric modification, and the modeling of ionosphere-magnetosphere interactions. Current research is strongly oriented toward understanding the spatial and temporal variability of the high-latitude ionsophere. Other research efforts include neutral winds and temperature in the equatorial F-region, interferometric measurement of winds in the high-latitude thermosphere, and theoretical studies of tidal motions in the upper atmosphere.

Analysis and interpretation of data acquired in the Magnetosphere-Ionosphere-Thermosphere Radar Studies (MITHRAS) observational phase continue to dominate the upper atmosphere program. The measurements were made between May 1981 and June 1982 by three incoherent scatter radars: Chatanika (Alaska), Millstone Hill (Massachusetts), and the European Incoherent Scatter (EISCAT) radar in Norway. Other measurements included in the analysis are from the NASA Dynamics Explorer (DE) satellite, the Scandinavian Twin Auroral Radar Experiment (STARE), and the worldwide magnetometer network. The MITHRAS effort is leading to greater understanding of the temporal and spatial variations of the upper atmosphere. Specific topics being addressed in the analysis include ion convection, discrete and diffuse aurorae, the mid-latitude trough, field-aligned currents, and neutral winds. The observational results are being compared with numerical models to improve the capability of modeling the ionosphere.

The need to compare model calculations with experimental data and the difficulties and costs of obtaining and interpreting upper atmospheric data dictate that advances in knowledge will be closely tied to observational capabilities. Current and planned instrumentation capabilities include the line of incoherent scatter radars between Sondre Stromfjord, Greenland, and Jicamarca, Peru; the NASA Upper Atmosphere Research Satellite (UARS); and the continuing opportunities afforded by the Space Shuttle. Theory and observations continue to support each other, as each poses problems or establishes requirements for the other. The results of this research may be expected to improve understanding of the environment in which aerospace systems operate and of the effects of Air Force operations on the environment.

RESEARCH EFFORTS COMPLETED IN FY 84

COMPLETED PROJECT SUMMARY - CHEMICAL TECHNIQUES
DENTON W. ELLIOTT

Electrochemistry and Electrochemical Methodology in Molten Salts
AFOSR-81-0007

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COMPLETED PROJECT SUMMARY

TITLE: Electrochemistry and Electrochemical Methodology in Molten Salts

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INCLUSIVE DATES: 1 October 1980 - 31 August 1984

GRANT NUMBER: AFOSR-81-0007

COSTS AND FY SOURCE: $120,000, FY 81; $120,000, FY 82; $120,000, FY 83

SENIOR RESEARCH PERSONNEL:

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JUNIOR RESEARCH PERSONNEL: T. Zawodzinski

PUBLICATIONS:

"Electrochemical Studies in Low Temperature Molten Salt Systems Containing Aluminum Chloride," B. J. Welch and R. A. Osteryoung, J. Electroanal. Chem., 118, 455 (1981).

"A Titration Procedure for the Determination of Oxide in Basic N-Butylpyridinum Chloride:Aluminum Chloride Melts," Z. Stojek, H. Linga, and R. A. Osteryoung, J. Electroanal. Chem., 119, 365 (1981).

"Electrochemistry of Ti(IV) in Basic N-Butylpyridinium Chloride and Aluminum Chloride in the Presence of Oxide," H. Linga, Z. Stojek, and R. A. Osteryoung, J. Am. Chem. Soc., 103, 3754 (1981).

"Substituent Effects in Iron Diimine Complexes: Correlations with Thermodynamic Properties in a Room Temperature Molten Salt," H. L. Chum, D. Koran and R. A. Osteryoung, Inorg. Chem., 20, 3304 (1981).

"Electrochemical and Spectroscopic Studies of 9,10-Anthraquinone in a Room Temperature Molten Salt," G. T. Cheek and R. A. Osteryoung, J. Electrochem. Soc., 129, 2488 (1982).

"Electrochemical Studies of Fe(II) and Fe(III) in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid," C. Nanjundiah, K. Shimizu, and R. A. Osteryoung, J. Electrochem. Soc., 129, 2474 (1982).

"Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System," G. T. Cheek and R. A. Osteryoung, Inorg. Chem., 21, 3581 (1982).

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"Electrochemical Studies of Sb(III) and Sb(V) in Molten Mixtures of Aluminum Chloride and Butylpyridinium Chloride," D. A. Habboush and R. A. Osteryoung, Inorg. Chem., 23, 1726 (1984).

"Electrochemical Studies in Room Temperature Molten Salts," R. A. Osteryoung, R. J. Gale, J. Robinson, R. Bugle and B. Gilbert in "Proceedings of the Second International Symposium on Molten Salts," J. Braunstein and R. Selman, Eds., The Electrochemical Society, Pennington, NJ (1981).

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"Electrochemical Studies in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid," C. Nanjundiah, K. Shimizu and R. A. Osteryoung in "Proceedings of the Workshop on Thermally Regenerative Electrochemical Systems," SERI/CP-234-1577, Solar Energy Research Institute, Golden, Colorado (1982).

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"High and Room Temperature Haloaluminates," R. J. Gale and R. A. Osteryoung in Molten Salt Techniques, D. Lovering and R. J. Gale, Eds., Plenum Press, New York (1983).

"Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System," G. T. Cheek and R. A. Osteryoung, Inorg. Chem., 21, 3581 (1982).

"Increased Electrochemical Window in Ambient Temperature Ionic Liquids," M. Lipsztajn and R. A. Osteryoung, J. Electrochem. Soc., 130, 1968 (1983).

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"On Determination of Equilibrium Constants for the Tetrachloroaluminate Dissociation in Ambient Temperature Ionic Liquids," Z. Karpinski and R. A. Osteryoung, Inorg. Chem., 23, 1491 (1984).

"Polymer Coated Electrodes in Ambient Temperature Ionic Liquids," P. G. Pickup and R. A. Osteryoung, J. Electrochem. Soc., 130, 1965 (1983).

"Electrochemical and Spectroscopic Studies of Polypyridine Complexes of Fe(II)/(III) and Ru(II)/(III) in the Aluminum Chloride N-(1-Butyl)pyridinium Chloride Molten Salt System," S. Sahami and R. A. Osteryoung, Inorg. Chem., 23, 2511 (1984).

"Electrochemical Polymerization of Pyrrole and Electrochemistry of Polypyrrole Films in Ambient Temperature Molten Salts, P. G. Pickup and R. A. Osteryoung, J. Am. Chem. Soc., 106, 2294 (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of work carried out under this grant was to perform chemical and electrochemical studies in ambient temperature ionic liquids (molten salts); these molten salt systems consisted of mixtures of either N-(1-butyl)pyridinium chloride (BuPyCl) or 1-methyl-3-ethyl-imidazolium chloride (ImCl) with aluminum chloride. The organic chlorides will be generalized as RCl. Work performed can be divided into three areas.

The first involved studies of solute chemistry in the BuPyCl-$AlCl_3$ and ImCl-$AlCl_3$ solvent systems, with particular interest in the effect of the solvent acidity (mole ratio of the organic chloride to aluminum chloride) on the redox properties of various solutes. Work carried out in this area involved: (a) studies of Al deposition; (b) electrochemistry of the Ti(III)/Ti(IV) couple, which, as a result of the interaction of Ti(IV) with oxide was developed into a method for the determination of oxide in a basic (excess RCl) containing melt; (c) electrochemistry of two related organic compounds, anthraquinone and chloranil (tetrachlorobenzoquinone); (d) electrochemical studies of the Fe-Fe(II)-Fe(III) system, including elucidation of complex ion formation and an indication of significant structural changes in the basic melt from the observation that the BuPyCl-$AlCl_3$ viscosity increased markedly in the basic melt; (e) electrochemical studies of the Cu-Cu(I)-Cu(II) system, again involving information relating to complex ion formation; (f) electrochemical study of the behavior of water in these molten salt systems and determination of water, which reacts to form HCl and an -Al-O-H species of some type, by rotating disc voltammetry; (g) studies of the I(0)-I(-1) and I(+1) redox system in the acidic melts; and (h) studies of the Sb-Sb(III)-Sb(V) couple, again with respect to complex ion formation and identification.

In a number of these cases it was found that the Stokes-Einstein equation was obeyed, and this could be employed to give credance to the structure of complex ions formed in the acidic and basic regions of melt composition.

The second area in which work was performed involved studies related to properties of the solvent system. The work included: (a) preparation of a new melt, composed of a substituted alkylpyridinium chloride and aluminum chloride; (b) discovery of a characteristic of the 1.00:1.00 mole ratio $AlCl_3$:RCl melts - a "neutral" melt - that results in extremely large voltammetric windows. This window is ca. 4.5 volts in the ImCl-$AlCl_3$ 1.00:1.00 melt; (c) utilization of the neutral melt for the study of the oxidation of chloride under very controlled conditions and the determination of complex ion stoichiometry by means of what is essentially an amperometric titration; (d) a reinvestigation of the dominant melt equilibrium,

$$2\ AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

for both the BuPyCl-$AlCl_3$ and the ImCl-$AlCl_3$ melts and the finding that the equilibrium constants for both are approximately the same, having a pK value of approximately 17.

The third area in which work was performed involved studies related to the behavior of polymer electrodes in the molten salt system. Work performed included: (a) showing that redox polymers, such as polyvinylferrocene, and others, although not prepared in the melt had excellent voltammetric behavior when used in the melt, with characteristics similar to those reported in other solvents; (b) a study of iron and ruthenium polypyridine complexes to ascertain if the redox chemistry of the solute species in the molten salt was similar to that of the redox couple when incorporated into a polymer in the melt; (c) studies of the electropolymerization of pyrrole and the electrochemistry of polypyrrole in the melt. This work indicated that the polypyrrole electrochemistry appears more facile in these melts than in other solvents studied to date.

RESEARCH EFFORTS COMPLETED IN FY84

COMPLETED PROJECT SUMMARY - SURFACE CHEMISTRY
CAPTAIN LEE E. MYERS

Structure of Solid Surfaces in
Wear Situations
AFOSR-81-0005

James L. Lauer
Dept. of Mechanical Engineering
Aeronautical Engnrng & Mechanics
Rensselaer Polytechnic Institute
Troy, NY 12181

COMPLETED PROJECT SUMMARY

TITLE: Structure of Solid Surfaces in Wear Situations

PRINCIPAL INVESTIGATOR: Dr. James L. Lauer
Department of Mechanical Engineering
Aeronautical Engineering and Mechanics
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INCLUSIVE DATES: 1 December 1981 - 30 June 1984

GRANT NUMBER: AFOSR-81-0005

COSTS AND FY SOURCE: $85,555, FY 81; $101,995, FY 82; $89,000, FY 83

JUNIOR RESEARCH PERSONNEL:

S. S. Fung
P. Vogel
M. Mailloux
M. Marxer

PUBLICATIONS:

"Analysis of Aircraft Fuel Line Deposits by Polarization Infrared Fourier Micro-Emission Spectrophotometry," J. L. Lauer and L. E. Keller, Applications of Surface Science, 9, 175 (1982).

"Microscopic Contour Changes of Tribological Surfaces by Chemical and Mechanical Action," J. L. Lauer and S. S. Fung, ASLE Transactions, 26, 430 (1983).

"Oxidized Aircraft Fuel Deposits on Metal Surfaces by Polarization-Modulated Infrared Fourier Emission Microspectrophotometry," J. L. Lauer and L. E. Keller, Applications of Surface Science, 15, 50 (1983).

"Emission FTIR Analyses of Thin Microscopic Patches of Jet Fuel Residues Deposited on Heat Metal Surfaces," J. L. Lauer and P. Vogel, Applications of Surface Science, 18, 182 (1984).

"Topological Reaction Rate Measurements Related to Scuffing," J. L. Lauer, S. Fung, and W. R. Jones, Jr. (NASA-Lewis), American Society of Lubrication Engineers, Preprint No. 83-LC02B01 (1983).

"Optical and Other Properties Changes of M-50 Bearing Steel Surfaces for Different Lubricants and Additives Prior to Scuffing," J. L. Lauer, N. Marxer, and W. R. Jones, Jr., American Society of Lubrication Engineers, Preprint No. 84-LC-2A-3 (1984).

"Emission FTIR Analyses of Jet Fuel Deposits," J. L. Lauer and P. Vogel, American Chemical Society, Preprints Symposium General Papers, Philadelphia, PA, 29, 1015 (Aug 1984).

"Analysis of Patchy Microscopic Depositions from Jet Fuels on Stainless Steel and Aluminum by IR Emission," J. L. Lauer and P. Vogel, Proceedings of the Third International Conference on Infrared Physics, W. Ruegsegger and F. K. Kneubuhl, Eds., 678 (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Identification and understanding of the surface phenomena involved in lubrication and wear are necessary if failures are to be avoided or at least mitigated. Failure of lubrication and high wear rates can be very costly to both civilian and military machinery.

While many new methods of surface analysis have been developed in recent years, their requirements of ultrahigh vacuum and of electron bombardment make these methods destructive. Furthermore they mostly furnish only elemental analysis and then their spatial resolution is not high. For some of our work we have been fortunate in having access to a scanning Auger electron spectrophotometer (AES); its best spatial resolution of about 50 μm is rather high. However, most of our analyses were carried out with spatial resolutions better than 20 m and they made use of (i) a phase-locked interference microscope (PLIM), (ii) an electronic Faradaymodulated ellipsometer (EFME), (iii) speckle-contrast (SC), and (iv) friction and lubricant thickness measurements with a ball-on-plate sliding contact. All this apparatus was of our ultimate design and it was assembled and completed in the search for significant surface changes in a bearing operated on its way to failure--except for SC, which was studied for applicability to metal-gas reactions. The design and construction of the PLIM and the EFME are major accomplishments of this project.

A realistic system was selected for these wear studies; an operating bearing contact consisting of a loaded M-50 bearing steel ball-on-plate mock-bearing and lubricants simulating MIL 23699 and its additives, i.e. a most common heavily loaded bearing system. The mock-bearing had dimensions such that the width of the wear track was amenable to our surface analyses.

Significant changes were found (i) in the changes of the surface profile within the wear track over the course of bearing operation for different lubricants, (ii) in the rate of oxidation of the steel bearing surface within and without the wear track after a brief exposure to dilute hydrochloric acid, and (iv) in the friction for different lubricants. Common surface additives in lubricants, such as tricresylphosphate (antiwear) and benzotriazole (anticorrosion), produced larger profile changes then other common lube additives. Invariably these changes could be associated with the more rapid formation of surface oxides within than without the wear track.

The hydrochloric acid probe reaction changing the surface profile could become a convenient and useful test for bearing surface reliability.

The PLIM and EFME instruments developed for this work will prove to be useful in many different applications, not only in the analysis of metal and metal oxide surfaces. The applicability of SC to reaction studies will, however, remain limited to gross changes. For these it can be used from large distances.

As part of this project, but in a separate investigation, jet fuel deposits formed on surfaces of a Jet Fuel Oxidation Tester (JFTOT) were analyzed by infrared emission Fourier microspectrophotometry, a technique we developed under a previous AFOSR grant.

RESEARCH EFFORTS COMPLETED IN FY 84

COMPLETED PROJECT SUMMARIES - CHEMICAL STRUCTURES
DONALD R. ULRICH

The Effect of Structure on Physical Properties of Polymers AFOSR-80-0101	Frank E. Karasz Polymer Science and Engineering University of Massachusetts Amherst, MA 01003
Preparation and Properties of Halide Glasses and Glass-Polymer Composites F49620-83-K-0003	John D. Mackenzie Materials Science and Engineering Department Univ. of California, Los Angeles Los Angeles, CA 90024
Laser Beam Technology Promoting High Speed and Selective Plating Processes AFOSR-82-0236	Joseph Zahavi Israel Institute of Metals Technion, Haifa 32000, Israel

COMPLETED PROJECT SUMMARY

TITLE: The Effect of Structure on Physical Properties of Polymers

PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
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INCLUSIVE DATES: 1 January 1980 - 30 September 1982

GRANT NUMBER: AFOSR-80-0101

COSTS AND FY SOURCE: $38,000 FY 80; $83,625 FY 81; $151,517 FY82

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V. Chacko
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J. Schroeder
S. Zacharius

PUBLICATIONS:

"Heats of Polymer Mixing," F. E. Karasz and W. MacKnight, Pure and Appl. Chem., 52, 409 (1980).

"Compatibility and Tensile Properties of PPO Blends," F. E. Karasz, J. Fried, and W. MacKnight, Polymer Alloys. II, D. Klempner and K. Frisch, Eds., Plenum Press, New York (1980).

"Dielectric Relaxation of Poly(chlorostyrenes) and their Copolymers," F. E. Karasz, P. Alexandrovich, and W. MacKnight, Polymer, 21, 488 (1980).

"Physical Properties of Compatible Polymer Mixtures," F. E. Karasz and W. MacKnight, Structure and Properties of Amorphous Polymers, A. Walton, Ed., Elsevier Publishing, Amsterdam (1980).

"Dielectric Studies of Polymer Compatibility: Blends of Polystyrene/ Poly-2-Chlorostyrene," F. E. Karasz, P. Alexandrovich, and W. MacKnight, J. Macromol. Sci. - Phys., B17, 501 (1980).

"The Interactions of Water with Epoxy Resins," F. E. Karasz and P. Moy, Water in Polymers, S. Rowland, Ed., ACS Symposium Series No. 127, Washington, D.C. (1980)

"Modified Sample Pans for Use in a Perkin-Elmer DSC-2", F. E. Karasz, J. Illinger, and N. Schneider, Thermo. Acta., 41, 51 (1980).

"Depolarized Dynamic Light Scattering of a Rigid Macromolecule Poly(p-phenylene benzbisthiazole)," F. E. Karasz, C. R. Crosby, III, N. C. Ford, Jr., and K. H. Langley, J. Chem. Phys, 75, 9 (1981).

"Solid State Transitions in Polymer Blends," F. E. Karasz, Kem. Ind., 31, 193 (1982).

"Compatibility Study of Fluorosubstituted Styrene with Poly(2,6-Dimethyl-1,4-Phyenylene Oxide) and with Polystyrene," F. E. Karasz, R. Vukovic and W. MacKnight, Hemi. Ind. (Yugoslavia), 35, 361 (1981).

"The Investigation of the Compatibility and Phase Separation of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and Styrene-fluorosubstituted Styrene Copolymer Blends by Differential Scanning Calorimetry," F. E. Karasz, R. Vukovic, V. Kuresevic, and W. J. MacKnight, Thermochimica Acta, 54, 349 (1982).

"Solid State Properties of Polymer Blends," F. E. Karasz and W. J. MacKnight, Polymer Compatibility, K. Solc, Ed., MMI Press, Midland, Michigan (1982).

"Scaling Theory and Enthalpy of Mixing for Binary Fluids," F. E. Karasz and G. ten Brinke, J. Chem. Phys., 77, 5249 (1982).

"Dynamic Mechanical Behavior of Filled Polyethylenes and Model Composites," F. E. Karasz, V. P. Chacko, and R. J. Farris, Polym. Eng. Sci., 22, 968 (1982).

"Morphology of $CaCO_3$-Filled Polyethylenes," F. E. Karasz, V. P. Chacko, R. J. Farris, and E. L. Thomas, J. Polym. Sci., 20, 2177 (1982).

"The Influence of Thermal Properties on the Glass Transition Temperature in Styrene/Divinylbenzene Network-Diluent Systems," F. E. Karasz, T. S. Ellis, and G. ten Brinke, J. Appl. Polym. Sci., 28, 23 (1983).

"Compatibility of Some Fluorosubstituted Styrene Polymers and Copolymers in Blends with Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and with Polystyrene," F. E. Karasz, R. Vukovic, and W. J. MacKnight, J. Appl. Polym. Sci., 28, 219 (1983).

"An Improved Upper Bound for the Free Energy of a Single Chain Lattice Model," F. E. Karasz and G. ten Brinke, J. Chem. Phys., 78, 995 (1983).

"Conformational Stability of Deuterated Poly(B-Benzyl-L-Aspartate) in m-Cresol," F. E. Karasz, G. E. Gajnos, and D. C. Lu, Int. J. Biol. Macromol., 5, 53 (1983).

"Viscoelastic Characterization of Poly(Butylene Terephthalate) using Longitudinal Resonances," F. E. Karasz and R. K. Galkiewicz, J. Material Sci., 18, 721 (1983).

"Depression of Glass Transition Temperature of Polymer Networks by Diluents," F. E. Karasz, G. ten Brinke, and T. S. Ellis, Macromolecules, 16, 244 (1983).

"Compatibility of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)/Poly(Fluoro-styrene-Co-Chlorostyrene) Blends," F. E. Karasz, R. Vukovic, V. Kuresevic, N. Segudovic, and W. J. MacKnight, J. Appl. Polym. Sci., 28, 1379 (1983).

"Evidence for Critical Double Points in Blends of Polystyrene and Poly(o-chlorostyrene), F. E. Karasz, S. L. Zacharius, G. ten Brinke, and W. J. MacKnight, Macromolecules, 16, 381 (1983).

"Compatibility of Poly(p-fluorostyrene-co-o-fluorostyrene) with Poly(2,6-dimethyl-1,4-phenylene oxide) and Polystyrene, F. E. Karasz, R. Vukovic, and W. J. MacKnight, Polymer, 24, 529 (1983).

"The Interaction of Epoxy Resins with Water: A Quadrupole Echo Deuterium NMR Study," F. E. Karasz, L. W. Jelinski, J. J. Dumais, R. E. Stark, and T. S. Ellis, Macromolecules, 16, 1019 (1983).

"Thermally Induced Phase Separation in PPO Blends," F. E. Karasz, J. Polym. Alloys, in press.

"Scaling Theory, Volume of Mixing and Effect of Pressure," F. E. Karasz, J. Chem. Phys., in press.

"Heat Capacity Increments: Conformational Transitions in Polypeptides," F. E. Karasz, Biopolymers, in press.

"Phase Behavior in Copolymer Blends: Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and Halogen-Substituted Styrene Copolymers," F. E. Karasz, Macromolecules, in press.

"Tensile Properties of $CaCO_3$ Filled Polyethylene," F. E. Karasz, J. Appl. Polym. Sci., in press.

"Ordered Block Copolymers," F. E. Karasz, Ultrastructure, in press.

"The Effect of Sample Temperature Gradients on DSC Thermograms at the Glass Transition Temperature," F. E. Karasz, Analytical Calorimetry, in press.

"Semi-Flexible Directed Self-Avoiding Walks," F. E. Karasz, Macromolecules, in press.

"The Interaction of Epoxy Resins with Water: The Depression of Glass Transition Temperature," F. E. Karasz, Polymer, in press.

"The One-Dimensional n→o Vector Model and the Helix-Coil Transition," F. E. Karasz, J. Chem. Phys., in press.

"Equilibrium Melting Point Depression for Blends of Isotactic Polystyrene with Poly(2,6-Dimethyl Phenylene Oxide), F. E. Karasz, Macromolecules, in press.

"LCST Behavior in Polymer Blends: Compressibility and Directional Specific Interactions, F. E. Karasz, Macromolecules, in press.

"Comment on the Correct Polarization Factor for Light Scattering Photometers Employing Annular Detection," F. E. Karasz, Macromolecules, in press.

"Dynamic Light Scattering Study of Semidilute Solutions of a Stiff Chain Polymer, F. E. Karasz, Macromolecules, in press.

"A Polymer Blend Exhibiting Both Upper and Lower Critical Solution Temperature Behavior: Polystyrene/Poly(Orthochlorostyrene), F. E. Karasz, Adv. in Chem. Series, in press.

"Water Induced T_g Depression in Nylon 6," F. E. Karasz, J. Polym. Sci., Phys. Ed., in press.

"On the Kinetic Delay for the Melting of Polymer Crystals," F. E. Karasz, Macromolecules, in press.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

OBJECTIVES

This report covers the period 1 Jan 80 - 30 Sep 82. For the first twenty-one months the research undertaken was an extension of earlier AFOSR supported endeavors dealing mainly with the physical properties of polymer blends, the plasticization of epoxy and other network polymers by water and the characterization of stiff chain macromolecules by quasi-elastic light scattering. A number of other topics received attention, detailed below. On 1 Oct 81 the objectives of AFOSR 80-0101 were expanded; it became a Multiple Investigator Research Project (MIRP) with a new focus for that of producing novel ultrastructural assemblies of macromolecules with electrical properties of interest. Two Faculty Associates, Professors R. W. Lenz and H. H. Winter, both of the Chemical Engineering Department here, were incorporated into the supported research program. However work on the previously identified areas in the physical properties of polymers, carried out by the P.I., was also continued, and is discussed below. The ultrastructural research program was therefore only at a relatively early stage at the conclusion of the time frame covered by this report.

In the polymer blend research substantial progress was achieved in elucidating thermodynamic and structural factors underlying the phenomenon of miscibility in binary polymer systems. The effects of chemical structure, tacticity, molecular weight, temperature, and their components were investigated by a number of techniques including calorimetry, vapor absorption, inverse gas chromatography and by the establishment of binary or ternary phase diagrams for appropriate systems. These were typically poly(2,6-dimethyl phenylene oxide) (PPO) and a halogenated styrene polymer or copolymer. By the conclusion of the reporting period a fairly detailed understanding of these effects and some progress towards prediction of new effects, had been obtained.

The study of the plasticization of network polymers was prompted by an earlier study of the effect on water on epoxy resins. It was established that, contrary to some earlier suppositions, the relatively large depression in the glass transitions of epoxies by small amounts of absorbed water, could be accounted for by purely thermodynamic analysis and did not require, in particular, the concept of specific polymer-sorbate interactions. These ideas were extended, with some success, to other chemically cross-linked macromolecules.

The solution properties of the stiff chain macromolecule poly(p-phenylene benzbisthiazole) (PBT) were studied by depolarized forward scattering proton correlation spectroscopy (quasi-elastic light scattering). By this technique the persistence length and other important chain conformational parameters were obtained for the first time.

Other topics investigated include the properties of a novel composite in which ultrahigh molecular weight polyethylene is covalently bonded to filler particles, the conformational transitions in polypeptide systems and a number of theoretical problems.

As indicated above the MIRP project on ultrastructure was at a relatively early stage of development at the conclusion of this grant. Nevertheless progress had been on the synthesis of block copolymers with electrically active interior blocks and on the special processing achievable with extensional flow dies.

ACCOMPLISHMENTS

The research completed during the grant period is divided into the following areas. In most cases, complete details are presented in the referenced publications or preprints.

a. Polymer Blends - To understand the thermodynamic factors involving miscibility requires a knowledge of basic free energy of mixing data for the system. For some combinations of a halogenated polystyrene this was obtained from heat of solution measurements. Other information was derived from dielectric relaxation data and from mechanical measurement. The phase behavior of these polymers was extensively investigated. In general as the fraction of the halogenated styrene in the respective

copolymers is increased, the LCST (lower critical solution temperature) decreases. In the case of copolymers of two dissimilar halogenated styrene units a "window of compatibility" appears; a quantitative theory to account for this can now be used to calculate interaction parameters χ_{ij}, where i,j represent monomer units within the system. The significance of this development lies in the predictability of compatibility from the relatively easily determined χ_{ij}'s. Other systems have also been investigated, including the effect of tacticity in methacrylate polymers. Crystallinity in these systems has been studied.

b. Plasticization of Network Polymers - The interaction of water was studied with respect to the effect of the diluent on the glass transition temperature, T_g. It is known that for example in epoxy resins relatively small amounts of water produce large depressions in T_g. We were able to account for this effect purely in terms of thermodynamic factors, i.e. without the necessity of invoking "specific interactions." This treatment was extended to other network systems and theoretically. Quadrupole echo deuterium NMR studies have recently confirmed that the water in epoxies is relatively mobile.

c. Quasi-elastic Light Scattering - Dynamic (quasi-elastic) light scattering can be used to characterize macromolecules in terms of size, conformation and, in favorable circumstances, size distribution. A specific form of this technique, forward depolarized scattering, yields rotational relaxation information directly, and is thus of use with respect to anisotropic conformations. In our work, forward depolarized light scattering was used to measure persistence lengths (a measure of chain stiffness) in poly(p-phenylene benzbisthiazole). The properties of stiff chain polymers in more concentrated regimes was investigated in another study.

d. Novel Composites - The interface between filler particles and a macromolecular matrix plays a key role in determining the mechanical properties of the composite. A novel composite was obtained in which the matrix (ultra high molecular weight polyethylene) was covalently bound to the surface of the filler particles ($CaCO_3$; Al_2O_3). The properties of this system were intensively examined in a morphological and mechanical property study.

e. Ultrastructure

(1) Synthesis - The goal of this investigation has been to prepare block or graft copolymers which will form two distinct phases in the solid state, and in which one of the phases will be electrically conducting and the other not. To achieve this objective, the block or graft copolymers must be initially, at least, fusible or soluble so that well controlled and well characterized two-phase systems can be formed, and the phase structure must be maintained after doping one of the polymers to form the conducting phase.

One of the polymers for the conducting phase, which was selected for our initial study, was poly-2-vinylpyridine, PVP, which can be doped with

either iodine or TCNB. This polymer can be obtained as a "living polymer" by anionic initiators, so AB block copolymers were prepared with both polystyrene, PS, and polybutadiene, PB, as the A blocks, which form the insulating phase and PVP as the B block for the conducting phase.

The diblock copolymers prepared could be solution cast into films that contained well developed two phase systems, which could be clearly seen by electron microscopy after selectively obtaining either the PB phase with osmium tetraoxide, OsO_4, or the PVP phase with iodine or methyl iodide. Considerable control including phase inversion can be achieved over the phase morphology by the manner in which the film is obtained, as well as by variation of polymer composition.

A second polymer under investigation, which has the potential of developing on doping conductivities as high as those of doped polyacetylenes, is polyphenylene vinylene, PPV. In all previous investigations described in the literature, this polymer has not been prepared in sufficiently high enough molecular weights from doped films for conductivity studies. However, we have investigated a new polymerization reaction by which we have been able to obtain strong films of the polymer by solution casting and reacting a precursor polymer. These films could be doped with iondine to a metallic-like appearance; the conversion of the precursor film to the PPV film has been quantitatively achieved, and relatively high conductivities were obtained.

(2) Extensional Flow Processing - A new technique has been developed for subjecting small polymeric samples to well defined extensional strains. The sample is introduced between two metal plates which are coated with a lubricant fluid. The sample is squeezed when the metal plates are driven together at a prescribed rate. The lubricant reduces the shear stresses in the sample to a level which is negligibly small. The instrument allows for measuring the squeezing force as well as the squeezing rate. Transient equibiaxial extensional viscosities as measured in this new device have been obtained. This is the first time that such an extensional viscosity has ever been measured for a molten polymer. The technique was developed further and is now capable for stretching at high temperatures and at prescribed rates.

f. Other Investigations - Conformational transitions in stiff, hydrogen-bonded, helices in polypeptides were studied with respect to the effect of temperature, solvent composition and isotope substitution ($H \rightarrow D$).

COMPLETED PROJECT SUMMARY

TITLE: Preparation and Properties of Halide Glasses and Glass-Polymer Composites

PRINCIPAL INVESTIGATOR: Professor John D. Mackenzie
Materials Science and Engineering Department
University of California, Los Angeles
Los Angeles, CA 90024

INCLUSIVE DATES: 10 October 1982 - 30 September 1983

CONTRACT NUMBER: F49620-83-K-0003

COSTS AND FY SOURCE: $188,131, FY 83

SENIOR RESEARCH PERSONNEL:

Dr. J. Lau
Dr. H. Nazu
Dr. R. Almeida
Dr. T. Tsuchiya

JUNIOR RESEARCH PERSONNEL:

K. Kadokura
G. Moore
E. Pope
J. Yuen
E. Wu
M. Fu-Dine
K.C. Chen

PUBLICATIONS:

"New Chloride Glass in the NaCl-KCl-$ThCl_4$ System," J. D. Mackenzie and H. F. Hu, J. Non-Crystalline Solids, 51, 269 (1982).

"The Electroconductivity of Fluorozirconate and Chloro-fluorozirconate Glasses," J. D. Mackenzie and R. M. Almeida, J Mat. Sci, 17, 2533 (1982)

"Viscosity of Molten Fluorozirconates," J. D. Mackenzie and H. F. Hu, J. Non-Crystalline Solids, 54, 241 (1983).

"New Halide Glasses-Bromide Glasses Based on $ZnBr_2$," H. F. Hu, F. D. Ma, and J. D. Mackenzie, J. Non-Crystalline Solids, 55, 169 (1983).

"New Methods of Studying Disordered Solids, J. D. Mackenzie and J. Lau, J. de Physique, 12, C9-7 (1982).

"Structure and Properties of Thorium-Fluorozironate Binary Glasses," R. M. Almeida and J. D. Mackenzie, Proceeding of the XIII Int. Cong. Glass, 850 (1983).

"A Structural Interpretation of the Vibrational Spectra of Binary Flourohafnate Glasses," R. M. Almeida and J. D. Mackenzie, J. Chem. Phys., 78, 6502 (1983).

"The Effects of Oxide Impurities on the Optical Properties of Fluoride Glasses," J. D. Mackenzie and R. M. Almeida, J. Non-Crystalline Solids, 56, 63 (1983).

"Dielectric Breakdown of Glasses," T. Kawaguchi and J. D. Mackenzie, Repts. of Rs. Lab., Asahi Glass Co., 33, 89 (1983).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Research has been carried out on two families of solids. The first one involves fluoride, chloride and bromide glasses. The second one involves microporous silica glass impregnated with organic polymers as well as inorganic crystals. The viscosity, vibrational spectra, chemical durability, fiber preparation and effects on oxygen on the properties of fluorozirconates have been studied. A number of new halide glasses were discovered. Microporous silica glass impregnated with PMMA was found to be highly transparent in the visible and possesses abnormal properties. Many crystals impregnated into silica glass were found to have their melting points depressed and some crystallographic transitions were also suppressed.

COMPLETED PROJECT SUMMARY

TITLE: Laser Beam Technology Promoting High Speed and Selective Plating Processes

PRINCIPAL INVESTIGATOR: Dr. Joseph Zahavi
Israel Institute of Metals
Technion, Haifa 32000, Israel

INCLUSIVE DATES: 1 September 1982 - 31 August 1984

GRANT NUMBER: AFOSR-82-0236

COSTS AND FY SOURCE: $35,000, FY82

JUNIOR RESEARCH PERSONNEL: S. Tamir

PUBLICATIONS:

"Laser Beam Technology Promoting High Speed and Selective Plating Processes,", J. Zahavi and S. Tamir, AFWAL-TR-83-4113 (Sep 83).

"Laser Beam Inducing Selective Plating Processes on GaAs Semiconductor Substrates," J. Zahavi and M. Halliwell, Proceedings of 11th International Congress on Metal Finishing Interfinish '84, Jerusalem, Israel, 21-26 October 1984.

"Laser Induced Metallization on Semiconductor Substrates," J. Zahavi and M. Halliwell, Plating and Surface Finishing Journal, to be submitted.

"Laser Induced Metallization on Semiconductor Substrates," J. Zahavi, International Conference on Metallurgical Coatings, San Diego, CA, 9-13 April 1984.

"Laser Gold Deposition on Polyimide," J. Zahavi, 11th International Conference on Metal-Finishing Interfinish '84, Jerusalem, Israel, 21-26 October 1984.

"Laser Induced Electrodeposition on Polyimide and GaAs Substrates," J. Zahavi, AFWAL-TR-83 (Aug 83), to be published.

"Laser Induced Electrodeposition on GaAs as Semiconductor," J. Zahavi, AFWAL-TR-83 (Aug 83), to be published.

PATENT APPLICATION:

"Laser Induced Deposition on GaAs," J. Zahavi and M. Halliwell.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Objectives

a. To study the promotion of high speed, high selective chemical and electrochemical plating processes induced by laser beam technology on metallic and non-metallic substrates.

b. To characterize deposits growth rate, structure, morphology, composition and stability as function of their formation condition (type, mode and intensity of the laser beam as well as mode and type of the electrolyte used).

c. To gain additional and better understanding of the mechanism and processes responsible and associated with laser induced chemical and electrochemical deposits on metallic and non-metallic substrates.

Accomplishments

a. Direct high speed high selective laser induced deposition of gold in the form of spots or lines on GaAs substrate from an aqueous solution of gold cyanide - proved feasible without recourse of external current supply and masking procedures. These findings indicate the possible mechanism of generating pairs of electrons-holes upon the interaction of the laser beam with the semiconductor surface and subsequently the consumption of these electrons by the gold ions in the solution to give deposit of metallic gold on the irradiated zones.

b. Direct high speed high selective laser induced palladium-nickel and gold deposits from electrolytic aqueous solutions on polymer substrates have been achieved. The mode through which these processes were taken place were believed to be involved with generating free electrons through bond breakage upon the interaction of the laser beam with the polymeric substrate. These free electrons were subsequently consumed by the gold or the palladium-nickel ions in the solution to give metallic deposition on the polymeric irradiated surface.

c. Laser induced selective electroless deposition of copper and nickel on polymeric substrate at laser irradiated zones. The main mechanism for these processes was basically involved thermal effects namely local temperature rise and subsequently high electroless deposition rate at laser irradiated zones.

RESEARCH EFFORTS COMPLETED IN FY84

COMPLETED PROJECT SUMMARIES - MOLECULAR DYNAMICS
CAPTAIN LEE E. MYERS

Rates of Intramolecular Conversions Over Low Barriers AFOSR-80-0046	Simon H. Bauer Department of Chemistry Cornell University Ithaca, NY 14853
Study of Molecular Lasers AFOSR-81-0028	George Burns Department of Chemistry Lash Miller Chemical Laboratories University of Toronto Toronto, Ontario M5S 1A1
Ion Photofragment Spectroscopy: Structure and Dissociation of Molecular Ions F46920-81-K-0006	Philip C. Cosby J. R. Peterson SRI International 333 Ravenswood Ave Menlo Park, CA 94025
Collisional Energy Exchange in Polyatomic Molecules F49620-83-K-0017	John B. Fenn Subbarao B. Ryali Department of Chemical Engineering Yale University New Haven, CT 06520
Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties F49620-83-C-0010	Robert W. Field James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Computer Modeling of Pulsed Chemical Lasers AFOSR-80-0003	Ronald L. Kerber Division of Engineering Research Michigan State University East Lansing, MI 48824
Study of Singlet Oxygen-Pentavalent Phosphorous Reactions F46920-82-C-0045	Leonard J. Marabella TRW Space & Technology Group 1 Space Park Redondo Beach, CA 90278
Electronically Excited Atomic and Molecular Oxygen AFOSR-79-0088	E. A. Ogryzlo Department of Chemistry University of British Columbia Vancouver, Canada V6T 1Y6

Theory and Experiments on Chemical Instabilities
AFOSR-81-0125

John Ross
Department of Chemistry
Stanford University
Stanford, CA 94305

Photoionization Investigation of Iodine Molecules and Clusters in a Supersonic Molecular Beam
AFOSR-83-0183

Edward A. Walters
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

COMPLETED PROJECT SUMMARY

TITLE: Rates of Intramolecular Conversions Over Low Barriers

PRINCIPAL INVESTIGATOR: Dr. Simon H. Bauer
Department of Chemistry
Cornell University
Ithaca, NY 14853

INCLUSIVE DATES: 1 January 1980 - 31 December 1983

GRANT NUMBER: AFOSR-80-0046

COSTS AND FY SOURCE: $45,326, FY 80; $29,430, FY 81; 60,000, FY 82;
$63,900, FY 83

SENIOR RESEARCH PERSONNEL: Dr. K. I. Lazaar

PUBLICATIONS:

"Intramolecular Unsymmetrical OHO Bonds. Thermochemistry," K. I. Lazaar and S. H. Bauer, Journal of Physical Chemistry, 87 2411 (1983).

"Second Order Rate Constants for Intramolecular Conversions: Application to Gas-Phase NMR Relaxation Times," S. H. Bauer and K. I. Lazaar, Journal of Chemical Physics, 79, 2808 (1983).

"Intramolecular Conversion Rates over Low Barriers II. The Alkyl Nitrites," K. I. Lazaar and S. H. Bauer, Journal of Physical Chemistry, to be published.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In this project the following objectives were the focus: (1) To test the applicability of RRKM unimolecular reaction rate theory to reactions with low activation energies, where the density of states is relatively low ($< 100/cm^{-1}$). We anticipated (and found) a limitation on the rate of intra-molecular vibrational energy redistribution for such sparsely spaced states. (2) To utilize our recognition of the fact that for low E_{act}'s the fall-off regime from first to second order kinetics occurs at relatively high pressures ($10-10^3$ Torr) depending on the presence or absence of low vibrational frequencies. Hence the observed rate can be pressure controlled. (3) To test whether gas phase NMR spectra, over a pressure range (10^3-10^0 Torr), covering the accessible temperature range (200-400°K) can be used to measure relaxation times for such species.

It was found that useful NMR spectra of gases, in which several species coexist in dynamic equilibrium, can be interpreted in terms of corresponding relaxation times, and that the tests for applicability of

RRKM can be made. We also obtained spectra of the reacting species in various solvents for comparison with the gas phase kinetic parameters. In particular, we investigated the following systems: (a) acetyl-acetones, (b) alkyl nitrites, (c) mixtures of dimethyl ether-hydrogen chloride, (d) formic and thioformic acids, and (e) inversion at the N atom in aziridine.

Finally, it is interesting to call attention to an "error" which appears in all published equations (with a single exception) for the limiting bimolecular reaction rate constant. As stated it is valid only for strictly non-reversible cases; a factor had been omitted from the integrand (in the final integration over energy) which should be included for reversible isomerizations. We presented a logical reformulation of the applicable kinetic equations, without reference to an ambiguous "transition state" model.

COMPLETED PROJECT SUMMARY

TITLE: Study of Molecular Lasers

PRINCIPAL INVESTIGATOR: Professor George Burns
Department of Chemistry
Lash Miller Chemical Laboratories
University of Toronto
Toronto, Ontario M5S 1A1

INCLUSIVE DATES: 1 November 1980 - 30 April 1984

GRANT NUMBER: AFOSR-81-0028

COSTS AND FY SOURCE: $14,365, FY 81; $34,145, FY 82; $35,425, FY 83

SENIOR RESEARCH PERSONNEL:

Dr. H. D. Kutz
Dr. W. H. Beck
Dr. R. K. Boyd
Dr. L. K. Cohen

JUNIOR RESEARCH PERSONNEL: T. C. Billard

PUBLICATIONS:

"Trajectory Study of Dissociation Reactions. The Single-Ensemble Method. II," H. D. Kutz and G. Burns, J. Chem. Phys., 74, 3947 (1981).

"Experimental Study of Dissociation-Recombination Reactions," R. K. Boyd and G. Burns, Shock Tube Chemistry, 131 (1981).

"Nonequilibrium Effects in the Energy Distribution Function," G. Burns and L. K. Cohen, J. Chem. Phys., 78, 3245 (1983).

"Time-Delayed Photoelectric Effect," T. C. Billard and G. Burns, Nature, 306, 247 (1983).

"Laser-induced Addition of Hydrogen Fluoride to Unsaturated Molecules. The HF + $C_2H_2CF_2$ System," W. H. Beck and G. Burns, Can. J. Chem., in press.

"The Effect of Large Energy Transfers Upon the Relative Nonequilibrium Effects," G. Burns and L. K. Cohen, in preparation.

"Bin Estimate Calculation of Errors in 3-D Trajectory Calculations," G. Burns and L. K. Cohen, in preparation.

"Trajectory Study of Nonequilibrium Effects in Diatom Dissociation Reactions," G. Burns and L. Kenneth Cohen, in preparation.

"Trajectory Study of Dissociation Reactions. The Single Ensemble Method III. Fluorine," G. Burns and L. K. Cohen, in preparation.

"Time-Delayed Photoemission," T. C. Billard and G. Burns, in preparation.

"Nonequilibrium Distribution Function of Irreversibly Dissociating F_2 in Ar," G. Burns and L. K. Cohen, in preparation.

"Trajectory Study of F_2 Dissociation at 1000 and 2000K," G. Burns and L. K. Cohen, in preparation.

"Characteristic Properties of Normalized Nonequilibrium Distribution Function Created in a Steady State Diatom Dissociation," G. Burns and L. K. Cohen, in preparation.

"The Validity of Information Theory in Diatom Dissociation Processes," G. Burns and L. Kenneth Cohen, in preparation.

"Calculation of Microcanonical Rate Constants using 3-D Trajectory Technique and the Single-Ensemble Method," G. Burns and L. K. Cohen, in preparation.

"Time-Delayed Photoelectron Emission Generated by Radiation Below Photoemission Threshold," T. C. Billard and George Burns, in preparation.

"Time-Delayed Photoemission in a GaAs(Cs,O) Photocathode," T. C. Billard and G. Burns, in preparation.

"Study in Molecular Lasers," G. Burns, Final Technical Report, 1984.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The initial objective of this research was, in part, the investigation of V-T, V-V, and V-R-T energy transfer in HF(v=5). Using a Quanta Ray Nd:YAG and a dye laser, HF(v=5) was detected photoacoustically. In order to observe HF(v=5) fluorescence, a far red sensitive end-on photomultiplier and Tektronix Transient Digitizer were used. Since much of the data sought were recently collected in the laboratories of Professors F. F. Crim (Univ. of Wisconsin) and F. Kaufman (Univ. of Pittsburgh), we concentrated on the reactivity of HF(v=5). For this purpose the laser induced addition of HF to several unsaturated molecules (C_2H_2, C_2H_4, C_2H_6, CH_2CH_2, and CF_2CClF) was attempted. Although there was no evidence of laser induced reaction products, the upper limit for the rate constant of the reaction HF + CH_2CF_2 was found to be 10^8 l $mol^{-1}sec^{-1}$ at 610K.

A time delayed photoemission (TDPE) from a trialkali photosensitive semiconductor was observed. For this purpose $Na_2KSb(Cs)$ photocathode of an RCA 7265 PMT was used. The details of the TDPE are still inadequately understood, and much work on this effect is being conducted in our laboratory.

Using 3-D trajectory calculations it was possible to define a new computational reaction kinetic "observable," $d^{SS}(E)$, the relative nonequilibrium energy distribution (RNED) function at the steady state. The $d^{SS}(E)$ is a plot of relative molecular densities of diatoms *vs.* their internal energies. The RNED, obtained as a histogram, proved to be significant for several reasons, one of which was that it can be described with a remarkedly high degree of precision by a simple algebraic function. The latter is calculated from known constants and physically meaningful constraints. It required only one adjustable parameter, *a*. For the case of Br_2 dissociation in Ar at 3500K, $a = 12.0 \pm 0.3$, which is intriguing because the transition state theory prescribes $a = +\infty$ for all reactions. Study of d(E) and of *a* might provide a novel method for testing the transition state and other quasi-equilibrium theories. Much work on this project is now being prepared for publication.

COMPLETED PROJECT SUMMARY

TITLE: Ion Photofragment Spectroscopy: Structure and Dissociation of Molecular Ions

PRINCIPAL INVESTIGATORS: Dr. P. C. Cosby
Dr. J. R. Peterson
SRI International
333 Ravenswood Ave
Menlo Park, CA 94025

INCLUSIVE DATES: 15 November 1980 - 28 February 1984

CONTRACT NUMBER: F49620-81-K-0006

COSTS AND FY SOURCE: $83,000, FY 81; $95,906, FY 82; $102,979, FY 83; $13,066, FY 84

SENIOR RESEARCH PERSONNEL: Dr. H. Helm
Dr. D. L. Huestis
Dr. R. P. Saxon

PUBLICATIONS:

"High Resolution Spectroscopy of $O_2^+(b^4\Sigma_g^-, v;=3,4,5 \leftarrow a^4\Pi_u, v'=3,4,5)$ Using Coaxial Laser and Ion Beams," P. C. Cosby, J. B. Ozenne, J. T. Moseley, and D. L. Albritton, J. Mol. Spectros., 79, 203 (1980).

"Observation of Predissociated Levels of CH^+," P. C. Cosby, H. Helm, and J. T. Moseley, Astrophys. J., 235, 52 (1980).

"Laser Predissociation Spectroscopy of the $f^4\Pi_g$ State of O_2^+," H. Helm, P. C. Cosby, and D. L. Huestis, J. Chem. Phys., 73, 2629 (1980).

"Photofragment Spectroscopy of O_3^+," J. T. Moseley, J. B. Ozenne, and P. C. Cosby, J. Chem. Phys., 74, 337 (1981).

"Laser Photofragment Spectroscopy of NO^+ I. Predissociation of the $2^3\Pi$ State," P. C. Cosby and H. Helm, J. Chem. Phys., 75, 3882 (1981).

"Photofragment Spectroscopy of N_2^{++}," P. C. Cosby, R. Moller, and H. Helm, Phys. Rev. A, 28, 766 (1983).

"Photofragment Spectroscopy of SO^+," P. C. Cosby, J. Chem. Phys., 80, XX (1984).

"Photofragment Spectroscopy of Shape Resonances in OH^+," H. Helm, P. C. Cosby, and D. L. Huestis, Phys, Rev. A., accepted.

"Photofragment Spectroscopy of CH_3I^+: Observation of Bimodal CH_3^+ Product Kinetic Energy Distributions," P. C. Cosby, Chem. Phys. Letter, in preparation.

"High Resolution Photofragment Spectroscopy of CH_3I^+," P. C. Cosby, Chem. Phys. Letter, in preparation.

"Photofragment Spectroscopy of O_2^+: Molecular Constants and Potential Energy Curve of the $f^4\Pi_g$ State," P. C. Cosby, D. L. Huestis, and H. Helm, J. Mol. Spectrosc., in preparation.

"Photofragment Spectroscopy of O_2^+: Predissociation Lifetimes of $f^4\Pi_g$ and Product State Distributions," H. Helm, D. L. Huestis, and P. C. Cosby, in preparation.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Molecular ions are prevalent in a wide range of gaseous media, including the earth's and other planetary atmospheres and ionospheres, interstellar space, gas discharges and lasers, MHD power generators, rocket exhaust plumes, and ballistic missile reentry wakes. A detailed knowledge of their structure and reactions is required in the development of both diagnostic techniques and theoretical models of the media.

The goal of this research was to apply the unique technique of photofragment spectroscopy to determine the structure and dissociation dynamics of small molecular ions. Our implementation of photofragment spectroscopy under this contract simultaneously employed sub-Doppler optical resolution and high dissociation fragment kinetic energy resolution. The technique is demonstrated to yield the identification, potential energy curves, and molecular constants of ion electronic states, precise bond dissociation energies and ionization potentials, excited state lifetimes, and product branching ratios. In particular, this research provides detailed information on the interactions among molecular electronic states and the partitioning of internal and translational energy in the dissociation process.

Over the course of this research, we applied the technique of photofragment spectroscopy to the ions O_2^+, NO^+, N_2^{++}, SO^+, OH^+, SH^+, and CH_3I^+. Our work on each of these species has provided new insights into the process of molecular dissociation dynamics and the inverse process of ion-atom collisions. One of the more notable achievements of this research was to observe for the first time a marked selectivity among atomic fine-structure states in a molecular dissociation, which has stimulated the introduction of new theoretical models to describe this process. The research has also provided the first experimental observation of a strong rotational dependence in the angular distribution of dissociation fragments, verifying a theoretical model introduced two decades earlier. In addition, it provided the first

definitive evidence for the existence of a stable doubly-charged diatomic ion that had been postulated nearly three decades ago, as well as spectroscopic identification of long-lived excited electronic states in ions produced by electron-impact ionization. Our work has further found that assumptions regarding the randomization of internal energy should not be routinely applied to all polyatomic ions.

COMPLETED PROJECT SUMMARY

TITLE: Collisional Energy Exchange in Polyatomic Molecules

PRINCIPAL INVESTIGATOR: Dr. John B. Fenn
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Yale University
P.O. Box 2159 YS
New Haven, CT 06520

INCLUSIVE DATES: 1 October 1979 - 31 December 1983

GRANT/CONTRACT NUMBER: F49620-80-C-0026 and F49620-83-K-0017

COSTS AND FY SOURCE: $53,700 FY 80; $72,874 FY 81; $80,736 FY 82; $88,053 FY 83

SENIOR RESEARCH PERSONNEL:

Gary L. Haller
Bret L. Halpern
Shi Da Shen
S. P. Venkateshan
Dhawan Sethi

JUNIOR RESEARCH PERSONNEL:

David A. Mantell
Yih Fen Maa
Moris Kori

PUBLICATIONS:

"Flowfield Calculations in Nonequilibrium Free Jets by the Method of Characteristics," M. Labowsku, S.B. Ryali, J.B. Fenn, and D.R. Miller in Rarefied Gas Dynamics (S.S. Fisher,ed.) Prog. in Astro. and Aero. 74, 695 AIAA (1981).

"Collisional Excitation of CO_2 by N_2, O_2 and Ar," S.B. Ryali, J.B. Fenn,C.E. Kolb and J.A. Silver, J. Chem. Phys. 76, 5878 (1982).

"Rotational Energy Distribution in CO_2 Vibrationally Excited by Collision with N_2," S.P. Venkateshan, S.B. Ryali, J.B. Fenn, Chem. Phys. Lett. 92, 606 (1982).

"Terminal Distributions of Rotational Energy in Free Jets of CO_2 by Infrared Emission Spectrometry," S. P. Venkateshan, S.B. Ryali, J.B. Fenn, J. Chem. Phys. 77, 2599 (1982).

"Distribution of Internal Energy in CO and CO_2 Scattered by a Hot Platinum Surface," D.A. Mantell, S.B. Ryali, & and J.B. Fenn, J. Chem. Phys. 78, 4250 (1983).

"Distribution of Internal Energy in NO Vibrationally Excited by a Hot Platinum Surface," D.A. Mantell, Y.-F. Maa, & and J.B. Fenn, J. Chem. Phys, 78, 6338 (1983).

"The Exciting Oxidation of CO on Pt," D.A. Mantell, S.B. Ryali, B.L. Halpern, G.L. Haller and J.B. Fenn, Chem. Phys. Lett. 81, 185 (1981).

"The Dynamics of CO Oxidation on Pt Deduced from Translational, Rotational and Vibrational Excitation in Product CO_2," D.A. Mantell, S.B. Ryali, G.L. Haller and J.B. Fenn, submitted to Surface Science.

"Time Resolved Infrared Emission Studies of CO_2 Formed by CO Oxidation on Pt and Pd," D.A. Mantell, S.B. Ryali and G.L. Haller, Chem. Phys. Lett. 102(1), 37 (1983).

"Vibrational Energy Distribution of CO in the Oxidation of C on Pt,"M. Kori and B.L. Halpern, Chem Phys. Lett 98, 32 (1983).

"Surface Catalyzed Production of N_2O from the Reaction of N Atoms and O_2 on Platinum," E. J. Murphy, J.B. Fenn and B.L. Halpern, J. Catal, 74, 434 (1981).

"Collision Kinetics in Gas Dynamics," J.B. Fenn in Applied Atomic Collision Pnysics, Vol 5 (E.W. McDaniel, ed.) Academic press (New York) 1982, p. 349.

"Order From Chaos with Molecular Beams," J.B. Fenn, Proc. Indian Acad, Sci. (Chem. Sci.), 89, 309 (1979).

"Where Are We Going With Molecular Beams," J.B. Fenn, Proc. 13th Rarefied Gas Dynamics Symposium (in press).

"Clusters as a Source of Error in Molecular Beam Scattering Experiments," H.L. Tien, S.B. Ryali, P.J. Gale and J.B. Fenn, Chem Phys. Lett. 93, 213 (1982).

"Further Reflections on the Role of a Mass Flux Gauge in the Calibration of Mass Spectrometeres for Dimers," J.B. Fenn, and N. Lee, Rev. Sci. Instr. 53, 1494 (1982).

"On the Time Required to Reach Fully Developed Flow," J.B. Fenn and K.J. Saenger, J. Chem. Phys. 79(12), 6043 (1983).

"Research Is Engineering," J.B. Fenn, Chem Eng. Educ., Fall 1982, 190.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Our objective has been to understand the details of energy exchange during encounters between polyatomic molecules in the gas phase and between such molecules and surfaces. In particular, we have been interested in the distribution of rotational and vibrational energy consequent to inelastic and reactive collisions. Information on these distributions is obtained by infrared radiometry and Fourier Transform Infrared Spectrometry (FTIS). The collisions that we study occur: (a) during expansion of supersonic free jets in vacuo; (b) when two such jets intersect each other as uncollimated molecular beams; (c) when one such jet is incident upon a surface. Following are some key results:

1. Terminal distributions of rotational energy in free jets of CO and CO_2 show a non-Boltzmann distribution that can be characterized by a two-temperature model and explained in terms of a competition between rotation-rotation and rotation-translation transfer.

2. Spectra of CO_2 molecules vibrationally excited by collisions with N_2 molecules at velocities up to 5 km/sec indicate a similar two-temperature distribution. A possible explanation is that the collision that excites vibration results in only a small amount of rotational excitation giving rise to the low temperature population. A second collision between vibrationally excited CO_2 and N_2 results in more rotational excitation that gives to the high temperature population.

3. There is substantial variation in excitation behavior when molecules are incident on a hot metal surface. Results with CO_2 show a probability of about 0.2 that the asymmetric stretch mode is excited. The rotational distribution of the vibrationally excited molecules is Boltzmann and corresponds to an accommodation of between 0.4 and 0.6. On the other hand, about 40% of the CO molecules reach complete vibrational accommodation with the surface and show a non-Boltzmann distribution of rotational energy corresponding to an overall rotational accommodation about the same as for CO_2.

4. Spectra of nascent CO and CO_2 molecules formed respectively by catalytic oxidation of C and CO on a platinum surface indicate internal "temperatures" substantially higher than the surface temperature. An energy balance indicates that only about 1/3 of the available reaction energy is absorbed by the surface. The remainder goes into excess translational, rotational and vibrational energy in the product molecules.

The idea of the experiment was to bring about the high energy collisions by opposing two uncollimated molecular beams (free jets in the free molecular flow regime). Each jet was obtained by expanding a mixture of one of the collision partners in hydrogen or helium. The intersection region of the two jets, where the high energy collisions occur, occupied the field of view of a senstive infrared detector. Collision energy was varied by changing the concentration of the seed species in the carrier gas. To a more cicumscribed extent, the source temperature could also be varied. There are two prerequisites in obtaining observable signals: molecules must become excited <u>and</u> they must radiate before they leave the field of view of the detector. This latter requirement compounds the problem of an already harassed experimenter because the radiative lifetimes of the expected states are at least several milliseconds. the residence time of an excited molecule in the field of view of the detector is of the order of a few times 10^{-5} seconds. The net result is that one can only hope to see a small fraction of the excited molecules, the impatient ones that radiate early. By painstaking attention to many small details such as alignment, optical focussing, careful baffling and improved calibration procedures, and after many frustrations and disappointments, we finally succeeded in increasing signal and reducing noise to the point where we could measure cross sections as small as a few times $10^{-20} cm^2$. We determined for the first time th TV cross section for the asymmetric stretch mode of CO_2 by collisions with N_2 and found that it rises steeply from a value of about $3 \times 10^{-20} cm^2$ at collision energies just above the threshold value of 0.288 eV to about $5 \times 10^{-17} cm^2$ at a collision energy of 2 eV. Most gratifying was the fact that measurements made when the jets intersect at 90 degrees were entirely consonant with those made when the intersection angle was 180 degrees. We also obtained cross sections for excitation of the same mode with argon, oxygen, and hydrogen as the collision partners. (1) We are now engaged in trying to carry out similar measurements with H_2O as the species to be excited.

These TV excitation cross sections were "total" in the sense that they related to all the radiation in the wavelength range of the InSb detector, 2 to 5 microns. It happens that for CO_2 the asymmetric stretch mode is the only one that can radiate in that interval. We then became interested in knowing the distribution of rotational energy in the collisionally excited molecules and were fortunate enough to obtain a Fourier Transform Infrared Spectrometer (FTIS) to see if we could spectrally resolve the radiation. This new task has proved to be inordinately more difficult than the measurement of total excitaton cross sections. In that case the detector was in the vacuum system only a few centimeters from the collision region. In the case of the FTIS experiment we had to "pipe" the radiation out of the vacuum system and through a window before it could enter the spectrometer. In addition, only a small fraction of the total radiation fell within the wavelength range for each of twenty or more rotational lines. After nearly a three years of trying, we finally obtained a useful spectrum for an optimum combination of collision velocity and flux density with CO_2 and N_2. (2) We will have to achieve further improvements in signal-to-noise before we can make measurements at other velocities.

The first elusive spectrum reveals a distribution that can best be described in terms of two sub-populations, one at a rotational temperature of 64K, the other at a temperature of 340K. Our tentative explanation is that the molecules in the low temperature group represent those which have had a single exciting collision with a N_2 molecule. We would expect low rotational energies for these molecules because only collisions with small impact parameter would put enough energy in the center of mass for vibrational excitation. The high temperature population comprises those molecules which have had a second collision after being vibrationally excited. Such a second collision would have a large probability of exciting higher J levels. We emphasize the tentative nature of this explanation of what we have observed. Further work will be required before we can claim any confidence in such a preliminary result.

COMPLETED PROJECT SUMMARY

TITLE: Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties

PRINCIPAL INVESTIGATORS: Dr. Robert W. Field
Dr. James L. Kinsey
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

INCLUSIVE DATES: 1 September 1980 - 30 September 1984

GRANT/CONTRACT NUMBERS: AFOSR 80-0254 and F49620 83-C-0010

COSTS AND FY SOURCE: $199,000, FY 81; $159,998, FY 82; $169,562, FY 83
$175,000, Fy 84

SENIOR RESEARCH PERSONNEL:

Dr. H.-L. Dai
Dr. Li Li
Dr. D. Katayama
Dr. J. Schmidt
Dr. H. S. Schweda
Dr. C. Kittrell
Dr. K. K. Innes
Dr. R. Redington

JUNIOR RESEARCH PERSONNEL:

D. E. Reisner
S. McDonald
R. F. Marks
M. Carrera
P. H. Vaccaro
G. K. Chawla
C. L. Korpa
A. Zabludoff

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

PUBLICATIONS:

"Rotation-Vibration Analysis of $B0_u^+$-$a1_g$ and $B0_u^+$-$a'0_g^+$ Electronic Systems of I_2 by Laser-Induced-Fluorescence Fourier-Transform Spectroscopy," S. Churassy, F. Martin, R. Bacis, J. Verges, and R. W. Field, J. Chem. Phys., 75, 4863 (1981).

"Tunable Laser Electronic Spectroscopy," R. W. Field, Disc. Faraday Soc., 71, 111 (1981).

"Assignments of the N_2 $W^3\Delta$-$B^3\Pi$ and $B^3\Pi$-$W^3\Delta$ Lasing Lines," D. Cerny, R. Bacis, R. W. Field, and R. A. McFarlane, J. Phys. Chem., 85, 2626 (1981).

"Selective Vibrational Excitation by Stimulated Emission Pumping," C. Kittrell, E. Abramson, J. L. Kinsey, S. McDonald, D. E. Reisner, D. Katayama, and R. W. Field, J. Chem. Phys., 75, 2056 (1981).

"Highly Excited, Normally Inaccessible Vibrational Levels by Sub-Doppler Modulated Gain Spectroscopy: The $Na_2 A\,^1\Sigma_u^+$ State," H. S. Schweda, G. K. Chawla, and R. W. Field, Opt. Commun., 42, 165 (1982).

"The CaO $D,d^{1,3}\Delta$-$a^3\Pi$ System: Sub-Doppler Spectrum, Rotational Analysis, and Deperturbation," R. F. Marks, R. A. Gottscho, and R. W. Field, Physica Scripta, 25, 312 (1982).

"The Orange Arc Bands of CaO: Analysis of a $D,d^{1,3}\Delta$-$a^3\Pi$ System," R. F. Marks, H. S. Schweda, R. A. Gottscho, and R. W. Field, J. Chem. Phys., 76, 4689 (1982).

"Selective Vibrational Excitation of Formaldehyde $\tilde{X}\,^1A_1$ by Stimulated Emission Pumping," D. E. Reisner, P. H. Vaccaro, C. Kittrell, R. W. Field, J. L. Kinsey, and H.-L. Dai, J. Chem. Phys., 77, 573 (1982).

"Laser Population of Highly Excited Vibrational Levels of Molecules," E. Abramson, H.-L. Dai, R. W. Field, D. G. Imre, J. L. Kinsey, C. Kittrell, D. E. Reisner, and P. H. Vaccaro, in Lasers as Reactants and Probes in Chemistry, W. Jackson, Ed., Howard University, 1982.

"Electric Dipole Moments of Excited Vibrational Levels in the $\tilde{X}\,^1A_1$ State of Formaldehyde by Stimulated Emission Spectroscopy," P. H. Vaccaro, J. L. Kinsey, R. W. Field, and H.-L. Dai, J. Chem. Phys., 78, 3659 (1983).

"Long Range Behavior of the Gerade States Close to the $^2P_{3/2}$ + $^2P_{3/2}$ Iodine Dissociation Limit by Laser-Induced Fluorescence Fourier-Transform Spectroscopy," F. Martin, S. Churassy, R. Bacis, R. W. Field, and J. Verges, J. Chem. Phys., 79, 3725 (1983).

"Direct Observation of High-Lying $^3\Pi_g$ States of the Na_2 Molecule by Optical-Optical Double Resonance," Li Li and R. W. Field, J. Phys. Chem., 87, 3020 (1983).

"Stimulated Emission Spectroscopy: A Complete Set of Vibrational Constants for $\tilde{X}\,^1A_1$ Formaldehyde," D. E. Reisner, R. W. Field, J. L. Kinsey, and H.-L. Dai, J. Chem. Phys., 80, 5968 (1984).

"Rotation Induced Vibrational Mixing in $\tilde{X}\,^1A_1$ Formaldehyde: Nonnegligible Dynamical Consequences of Rotation," H.-L. Dai, C. L. Korpa, J. L. Kinsey, and R. W. Field, J. Chem. Phys., to be published.

"State-Specific Rates of $H_2CO(S_0) \rightarrow H_2 + CO$ at Energies Near the Top of the Barrier: A Violation of RRKM Theory?", H.-L. Dai, R. W. Field, and J. L. Kinsey, J. Chem. Phys., to be published.

"Intramolecular Vibrational Dynamics Including Rotational Degrees of Freedom: Chaos and Quantum Spectra," H.-L. Dai, R. W. Field, and J. L. Kinsey, J. Chem. Phys., to be published.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A. Stimulated Emission Pumping Studies of Formaldehyde

The Stimulated Emission Pumping (SEP) technique was applied for the first time to a polyatomic molecule, H_2CO. SEP spectroscopy has provided an unprecedentedly complete picture of the structure of H_2CO at high levels of excitation. A complete set of anharmonic vibrational constants, ω_i and x_{ij}, was obtained from data on more than 80 vibrational levels at energies up to 9300 cm^{-1}. Nonrotating H_2CO is vibrationally well organized at $E \lesssim 9300$ cm^{-1}, but rotation causes significant mode mixing. This implies that structurally quite distinct nonrotating levels coexist with structurally indistinguishable rotating levels and that level-specific chemistry, if it will ever be observable, must compete with rotational thermalization. Measures of quantum ergodicity were applied to the H_2CO SEP spectra with the surprising result that, even though the spectra sample more levels as the rotational quantum numbers J and K are increased, a decreasing fraction of accessible phase space is sampled.

B. The $H_2CO(S_0) \rightarrow H_2 + CO$ Barrier

Stark Quantum Beat and $S_0 \sim S_1$ Anticrossing Spectroscopy were used to measure the homogeneous width of two S_0 rotation-vibration levels near the top of the S_0 barrier. A result at variance with simple RRKM theory was obtained: for two J = 2 levels separated by 31 cm^{-1}, the higher energy level penetrates the barrier a factor of 2.5 slower than the lower energy level. An upper bound to the S_0 barrier is obtained.

C Collisional Studies of H_2CO $\tilde{A}\ ^1A_1$

Two pulsed-cw variants of SEP, Transient Gain and Transient Polarization Spectroscopy enable measurement of single-J level collisional depopulation and depolarization rates and state-to-state transfer rates free of the multiple-collision effects and limited resolution of resolved fluorescence studies.

D Spectroscopic Studies of Na_2

Two new techniques were demonstrated. Modulated gain spectroscopy has allowed observation of the levels of the Na_2 $A^1\Sigma_u^+$ and $B^1\pi_u$ states near the Na (^2S) + Na(^2P) dissociation limit. Perturbation facilitated Optical-Optical Double Resonance has made the Na_2 triplet valence and Rydberg states accessible to sub-Doppler spectroscopy.

COMPLETED PROJECT SUMMARY

TITLE: Computer Modeling of Pulsed Chemical Lasers

PRINCIPAL INVESTIGATOR: Dr. Ronald L. Kerber
Division of Engineering Research
Michigan State University
East Lansing, MI 48824

INCLUSIVE DATES: 1 November 1981 - 31 October 1983

GRANT NUMBER: AFOSR-80-0003

COSTS AND FY SOURCE: $69,258, FY 81; $24,221, FY 82; $29,987 FY 83

JUNIOR RESEARCH PERSONNEL:

W. Jaul	T. Nees
P. Sojka	M. Brake
D. Stone	K. Emery

PUBLICATIONS:

"Time Resolved Specira and Small Signal Gain in HF: An Experimental and Theoretical Investigation," R. L. Kerber, P. E. Sojka, and W. K. Jaul, Proc. of the Fourth Intl Symp. on Gas Flow and Chemical Lasers, Stresa, Italy, 13-17 September 1982.

"A Study of the Effect of Vibrational to Rotational to Translational Relaxation Mechanisms in Pulsed H_2+F_2 Lasers," R. L. Kerber and R. C. Brown, Applied Optics, accepted.

"A Theoretical Assessment of the Kinetic Limitations of the Chemically Pumped HF Optical Resonant Transfer Laser," R. L. Kerber and W. K. Jaul, Report #MSU-ENGR-82-018, August, 1982.

"High-Performance DF-CO_2 Chain-Reaction Laser," R. L. Kerber, S. T. Amimoto, J. S. Whittier, G. Harper, R. Hofland, Jr., J. M. Walters, Jr., T. A. Barr, Jr., and W. K. Jaul, Air Force Systems Command Report No. SD-TR-83-05, February, 1983.

"A Theoretical and Experimental Investigation of the Chemical Kinetics of an Oxygen Microwave Discharge," M. L. Brake, Ph.D. Thesis, 1983.

"Time Resolved Spectroscopy and Small Signal Gain in a Flash Initiated Pulsed HF Laser," P. Sojka, Ph.D. Thesis, 1983.

Kerber

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A computer modeling study of pulsed H_2+F_2 and D_2+F_2 chemical lasers has been conducted. This work was directed toward understanding

the role of kinetic rotational relaxation and vibrational-rotational relaxation mechanisms in HF and DF lasers. This study resulted in very comprehensive computer models that could predict spectral characteristics of pulsed laser performance using kinetic rate equation data and experimental conditions.

In addition, experiments were conducted on a flash initiated pulsed H_2+F_2 laser facility to generate data to compare with the models developed in this study. Models were also developed that demonstrated the performance of pulsed laser driven amplifiers and optical resonance transfer lasers. Finally, simple models were constructed that permit efficient prediction of pulse energy and pulse power.

Model predictions continue to improve as our understanding of the kinetic mechanisms improves. It is felt that these models are sufficiently comprehensive in kinetic mechanisms that no future model development is required. However, this study has pointed out a need for two follow-on efforts.

a. The models should be expanded to include kinetics associated with $H_2/O_2/F_2$ mixtures since many systems use O_2 as a prereaction inhibitor.

b. More work is required to improve the comparison of the comprehensive model predictions with experiment.

COMPLETED PROJECT SUMMARY

TITLE: Study of Singlet Oxygen-Pentavalent Phosphorous Reactions

PRINCIPAL INVESTIGATOR: Dr. Leonard J. Marabella
TRW Space & Technology Group R1/1196
1 Space Park
Redondo Beach, CA 90278

INCLUSIVE DATES: 1 April 1982 - 31 May 1984

CONTRACT NUMBER: F49620-82-C-0045

COSTS AND FY SOURCE: $70,000, FY 82; $81,130, FY 83, $43,189, FY 84

SENIOR RESEARCH PERSONNEL: Dr. J. Kuper
Dr. J. A. Betts

JUNIOR RESEARCH PERSONNEL: C. Lovejoy

PUBLICATION:

"Study of Singlet Oxygen-Pentavalent Phosphorus Reactions," L. J. Marabella, J. Kuper, C. Lovejoy, and J. A. Betts, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Detailed studies of an atomic oxygen-singlet delta oxygen-dimethyl hydrogen phosphite gas phase reaction system have been performed. Decay of singlet delta oxygen was modeled and a reaction mechanism which explains the experimental observations was derived. Semilog plots of oxygen singlet delta emission intensities versus time obtained show an initial rise in the emission followed by a straight line decay. The mechanism that explains this is reaction of oxygen atoms with the phosphorus compound to form an intermediate species which quenches the oxygen singlet delta. Emission from the intermediate species explains the initial rise in intensity. It was also found that nitric oxide terminates the quenching of oxygen singlet delta, presumable by reaction of nitric oxide with the phosphorus intermediary. Addition of water to the flow resulted in no change in singlet delta emission time history. This indicates that oxygen singlet delta does not enhance the hydrolysis of the studied oxygen compounds.

COMPLETED PROJECT SUMMARY

TITLE: Electronically Excited Atomic and Molecular Oxygen

PRINCIPAL INVESTIGATOR: Professor E. A. Ogryzlo
Department of Chemistry
University of British Columbia
Vancouver, Canada V6T 1Y6

INCLUSIVE DATES: 1 March 1979 - 30 June 1984

GRANT NUMBER: AFOSR-79-0088

COSTS AND FY SOURCE: $70,000, FY 83; $36,000, FY 82; $34,426 FY81;
$33,280, FY80

SENIOR RESEARCH PERSONNEL: Dr. R. D. Kenner
Dr. P. T. Wassell

PUBLICATIONS:

"On the Excitation of the Night Airglow on Earth, Venus and Mars," R. D. Kenner, E. A. Ogryzlo, and S. Turley, J. Photochem., 10 199 (1979).

"Deactivation of $O_2(A^3\Sigma_u^+)$ by O_2, O and Ar," R. D. Kenner and E. A. Ogryzlo, Int. J. Chem. Kin., 7, 501 (1980).

"Excitation of the Green Line in the Night Airglow," R. D. Kenner, E. A. Ogryzlo, and P. T. Wessell, Nature, 291, 398 (1981).

"A Direct Determination of the Rate Constant for the Quenching of $O(^1S)$ by $O_2(a^1\Delta_g)$," R. D. Kenner and E. A. Ogryzlo, J. Photochem., 18, 379 (1982).

"Quenching of $O_2(c^1\Sigma_u^-)$ by $O(^3P)$, $O_2(a^1\Delta_g)$ and other Gases," R. D. Kenner and E. A. Ogryzlo, Can. J. Chem., 61, 921 (1983).

"Rate Constant for the Deactivation of $O_2(A^3\Sigma_u^+)$ by N_2," R. D. Kenner and E. A. Ogryzlo, Chem. Phys. Letts., 103, 209 (1983).

"Orange Chemiluminescence from Nitrogen Dioxide," R. D. Kenner and E. A. Ogryzlo, J. Chem. Phys., 80, 1 (1984).

"The Yield of $O_2(b^1\Sigma_g^+)$ in Oxygen Atom Recombination," E. A. Ogryzlo, Y. Q. Shen and P. T. Wessell, J. Photochem., 25, 389 (1984).

"Quenching of the $O_2(A\rightarrow X)$ Herzberg I Bands by $O_2(a^1\Delta_g)$," R. D. Kenner and E. A. Ogryzlo, Can. J. Phys., (Dec 84) to be published.

"Chemiluminescent Association Reactions in the Upper Atmosphere," E. A. Ogryzlo, Chemiluminescence and Chemionization, A. Fontijn, Ed., Marcel Dekker, Amsterdam (1984).

*Chemiluminescence in Gas Phase Reactions, R. D. Kenner and E. A. Ogryzlo, Chemiluminescence and Bioluminescence Today, J. G. Burr, Ed., Marcel Dekker, Amsterdam (1985).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this study was an understanding of the mechanism by which the principal features of the night airglow are excited at an altitude of 100 km in the atmospheres of Earth and Venus. This requires a determination of the rate laws governing the production of excited states of O_2 and O in the recombination atoms. Since nothing was known about the quenching characteristics of many of the electronically excited states of O_2, the initial phase of this work was an attempt to develop a method of producing them under conditions suitable for kinetic studies. Surface catalyzed recombination of oxygen atoms proved to be a useful device for this purpose and the quenching characteristics of $O_2(A^3\Sigma_u^+)$, $O_2(c^1\Sigma_u^-)$ and $O(^1S)$ were determined in this way. With these quantities established, the rate laws governing the production of $O_2(A^3\Sigma_u^+)$, $O_2(c^1\Sigma_u^-)$, $O(^1S)$, $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ were determined. In all cases these were found to be complex providing direct evidence for the formation of an unidentified precursor in the initial act of recombination. The magnitudes of the rate constants determined in each case indicated that this precursor is formed in high yield in oxygen atom recombination. Direct application of these rate constants to the upper atmosphere results in predicted emission intensities which are always lower than those observed in the night airglow. A complete understanding of the night airglow emissions continues to elude us.

COMPLETED PROJECT SUMMARY

TITLE: Theory and Experiments on Chemical Instabilities

PRINCIPAL INVESTIGATOR: Professor John Ross
Department of Chemistry
Stanford University
Stanford, CA 94305

INCLUSIVE DATES: 15 January 1982 - 14 January 1984

GRANT NUMBER: AFOSR-81-0125

COSTS AND FY SOURCE: $105,000, FY 82; $110,254, FY 83

SENIOR RESEARCH PERSONNEL:

Dr. C. Escher
Dr. M. Hatlee
Dr. S. Kai
Dr. J. Marqusee
Dr. S. Muller
Dr. P. Rehmus
Dr. P. Richter
Dr. G. Venzl

Visiting Faculty

Dr. C. C. Hunt
Dr. Frisch
Dr. P. Hunt

JUNIOR RESEARCH PERSONNEL:

J. Kramer
E. C. Zimmermann
P. M. Wood

PUBLICATIONS:

"Measurements of Temporal and Spatial Sequences of Events in Periodic Precipitation Processes," S. Kai, S. Muller, and J. Ross, J. Chem. Phys., 76, 1392 (1982).

"Thermodynamic Processes, Time Scales and Entropy Production," V. Fairen, M. D. Hatlee, and J. Ross, J. Phys. Chem., 86, 71 (1982).

"Nucleation and Colloidal Growth in Concentration Gradients (Liesegang Rings)," G. Venzl and J. Ross, J. Chem. Phys., 77, 1302 (1982).

"Comments on Pattern Formation in Precipitation Processes," G. Venzl and J. Ross, J. Chem. Phys., 77, 1308 (1982).

"Periodic Precipitation Patterns in the Presence of Concentration Gradients. 1. Dependence on Ion Product and Concentration Difference," S. C. Muller, S. Kai, and J. Ross, J. Phys. Chem., 86, 4078 (1982).

"Mesoscopic Structure of Pattern Formation in Initially Uniform Colloids," S. Muller, S. Kai and J. Ross, J. Phys. Chem., 86, 4294 (1982).

"Periodic Precipitation Patterns in Presence of Concentration Gradients. II. Spatial Bifurcation of Precipitation Bands and Stochastic Pattern Formation," S. Kai, S. Muller and J. Ross, J. Phys. Chem., 87, 806 (1983).

"The Periodically Forced Conversion of 2,3-Epoxy-1-Propanol to Glycerine: A Theoretical Analysis," P. Rehmus, E. C. Zimmermann, H. L. Frisch and J. Ross, J. Chem. Phys., 78, 7241 (1983).

"Kinetics of Phase Transitions: Theory of Ostwald Ripening," J. A. Marqusee and J. Ross, J. Chem. Phys., 79, 373 (1983).

"Critique of a Proposed Stability Criterion for Chemical Systems Far From Equilibrium," C. Escher and J. Ross, Proc. Natl. Acad. Sci. USA, 80, 3133 (1983).

"Comments on Two Treatments of Symmetry Rules in Chemical Reactions," H. Metiu, G. C. Schatz, and J. Ross, J. Chem. Phys., 79, 2854 (1983).

"Path Integral Solutions for Fokker-Planck Conditional Propagators in Non-Equilibrium Systems; Catastrophic Divergences of the Onsager-Machlup-Laplace Approximation," P. M. Hunt, K.L.C. Hunt, and J. Ross, J. Chem. Phys., 79, 3765 (1983).

"Multiple Ranges of Flow Rate with Bistability and Limit Cycles for Schlögl's Mechanism in a CSTR," C. Escher and J. Ross, J. Chem. Phys., 79, 3773 (1983).

"Commentary: Dissipation Regulation in Oscillatory Reactions - Application to Glycolysis," P. Richter and J. Ross, Aspects of Chemical Evolution Proceedings of the XVIIth Solvay Conf. on Chem., G. Nicolis, Ed., Wiley, NY (1983).

"Theory of Ostwald Ripening: Competitive Growth and Its Dependence on Volume Fraction," J. A. Marqusee and J. Ross, J. Chem. Phys., 80, 536 (1984).

"Light Induced Bistability in $S_2O_6F_2 \rightleftharpoons 2SO_3F$: Theory and Experiment," E. C. Zimmermann and J. Ross, J. Chem. Phys., 80, 720 (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was the theoretical and experimental study of chemical instabilities including experiments on macroscopic structure formation in chemical periodic precipitation processes, the theory of periodic precipitation processes, light induced bistability in $S_2O_6F_2$, dynamic fluctuations in optical bistability, dissipation and control in oscillatory reactions, stochastic theory of nonlinear irreversible processes, experiments on chemical waves, and related topics. We have carried out extensive experiments on macroscopic structure formation in periodic precipitation processes. We measured the temporal sequence of

events in Liesegang experiments and showed that nucleation is continuous in space followed by a focussing mechanism which leads to pattern formation. The experiments contradict the earlier Ostwald theory and substantiate our hypothesis that ring formation follows from a chemical instability, that of autocatalytic growth of colloidal particles coupled with diffusion. We have studied bistability in illuminated gas phase reaction mixtures of $S_2O_6F_2$. We observed bistability, tristability, chemical hysteresis, and sharp transitions between stable branches. We have studied dissipation and control in oscillatory chemical reactions for the purpose of analyzing entrainment bands in external perturbations of such reactions, resonance response at characteristic frequencies phase locking of chemical intermediates in the reaction to the external perturbation, and dissipation within entrainment bands. We establish the interesting possibility of distribution of dissipation among different irreversible processes such as reaction, diffusion, thermal conduction, etc. by means of external perturbations. Application of these theories is made to a study of glycolysis. An investigation has been made of the stochastic theory of nonlinear irreversible processes by means of path integral techniques.

COMPLETED PROJECT SUMMARY

TITLE: Photoionization Investigation of Iodine Molecules and Clusters in a Supersonic Molecular Beam

PRINCIPAL INVESTIGATOR: Dr. Edward A. Walters
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

INCLUSIVE DATES: 28 June 1983 - 28 February 1984

GRANT NUMBER: AFOSR-83-0183 (Minigrant)

COSTS AND FY SOURCE: $12,000, FY 83

JUNIOR RESEARCH PERSONNEL: E. T. Hui

PUBLICATION:

"Photoionization Investigation of Iodine Molecules and Clusters in a Supersonic Molecular Beam," E. A. Walters, Final Technical Report

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A nozzle was designed and constructed which is to produce clusters of iodine molecules and atoms in the gas phase. Preliminary tests and experiments with this nozzle were conducted. Molecular iodine was expanded through another nozzle in He carrier gas and photoionized in a mass spectrometer. A partial photoion yield curve for the production of iodine molecular ions was obtained for the wavelength regions of 1216-1254 Å and 1299-1346 Å at an optical resolution of 1.75 Å. The adiabatic ionization potential of molecular iodine was determined to be 9.308 ± 0.006 eV with a spin-orbit splitting to the next highest electronic energy state of 0.645 ± 0.006 eV (5214 ± 50 cm^{-1}). Many autoionization features were observed in the region above threshold, but because of the limited range of wavelengths studied they were not assigned to particular Rydberg states.

RESEARCH EFFORTS COMPLETED IN FY 84

COMPLETED PROJECT SUMMARIES - CHEMICAL REACTIVITY AND SYNTHESIS
ANTHONY J. MATUSZKO

New Approaches to the Synthesis of Novel Organosilanes AFOSR-80-0293	Philip Boudjouk Department of Chemistry North Dakota State University Fargo, ND 58105-5516
Effect of Toluene on the Solubility of Biohazardous Volatile Synthetic Organic Compounds AFOSR-83-0175	Ervin Hindin Civil & Environmental Engineering Washington State University Pullman, WA 99164
Structural and Synthetic Organosilicon Chemistry AFOSR-81-0185	Michael E. Jung Department of Chemistry Univ. of California, Los Angeles Los Angeles, CA 90024
Synthesis of a Series of Acetylene Terminated Olegomers: Structure Property Relationships AFOSR-83-0123	James J. Kane Department of Chemistry Wright State University Dayton, OH 45435
Polyphosphorus Compounds Containing Phosphorus-Nitrogen Bonds AFOSR-81-0051	R. Bruce King Department of Chemistry University of Georgia Athens, GA 30602
Mechanisms and Kinetics of Diphthalocyanine Electrode Processes. Electrochemistry of Rare-Earth Diphthalocyanines F49620-80-C-0060, F49620-83-C-0088	M. M. Nicholson Member of Technical Staff Rockwell Intl. Science Center Anaheim, CA 92803
Basic Research in Novel Inorganic Reagents and Fluorocarbon Chemistry F49620-81-C-0020	Carl J. Schack Karl O. Christe Rocketdyne Division Rockwell International Canoga Park, CA 91304
Structural and Dynamic Studies of Materials Possessing High Energy Content AFOSR-81-0013	Nicholas J. Turro Department of Chemistry Columbia University New York, NY 10027

COMPLETED PROJECT SUMMARY

TITLE: New Approaches to the Synthesis of Novel Organosilanes

PRINCIPAL INVESTIGATOR: Professor Philip Boudjouk
Department of Chemistry
North Dakota State University
Fargo, ND 58105-5516

INCLUSIVE DATES: 1 September 1980 - 31 October 1983

GRANT NUMBER: AFOSR-80-0293

COSTS AND FY SOURCE: $41,984, FY 80; $57,140, FY 81; $66,676, FY 83

JUNIOR RESEARCH PERSONNEL:

R. Soorlyakumaran
A. King
B.-H Han
M. Liddle
K. Anderson
D. Thompson
D. Falvey
U. Samaweera
P. Anfinrud

PUBLICATIONS:

"Organic Sonochemistry. Ultrasound-Promoted Coupling of Organic Halides in the Presence of Lithium Wire," B-H. Han and P. Boudjouk, Tetrahedron Lett., 22, 2757 (1981).

"Organic Sonochemistry. Ultrasound-Promoted Coupling of Chlorosilanes in the Presence of Lithium Wire," P. Boudjouk and B-H. Han, Tetrahedron Lett., 22, 3813 (1981).

"Organic Sonochemistry. Ultrasound-Promoted Reaction of Zinc with alpha, alpha'-Dibromo-o-xylene. Evidence of Facile Generation of o-Xylylene,' B-H. Han and P. Boudjouk, J. Org. Chem., 47, 751 (1982).

"Organic Sonochemistry. Ultrasonic Acceleration of the Reduction of Simple and Deactivated Aryl Halides Using Lithium Aluminum Hydride," B-H. Han and P. Boudjouk, Tetrahedron Lett., 23, 1643 (1982).

"Organic Sonochemistry. Sonic Acceleration of the Reformatsky Reaction," B-H. Han and P. Boudjouk, J. Org. Chem., 47, 5030 (1982).

"Sonochemical and Electrochemical Synthesis of Tetramesityldisilene," P. Boudjouk, B-H. Han and K. R. Anderson, J. Amer. Chem. Soc., 104, 4992 (1982).

"Palladium-Catalyzed and Sonically Accelerated Hydrogenations of Olefins Using Formic Acid as a Hydrogen Transfer Agent," P. Boudjouk and B-H. Han, J. Catalysis, 79, 489 (1983).

"Organic Sonochemistry. Ultrasonic Acceleration of the Hydrosilation Reaction," B-H. Han and P. Boudjouk, Organometallics, 2, 769 (1983).

"Are the Silacyclopentadienyl Anion and the Silacyclopropenyl Cation Aromatic?", M. S. Gordon, P. Boudjouk and F. Anwari, J. Amer. Chem. Soc., 105, 4972 (1983).

"Organische Chemie mit Ultraschall," P. Boudjouk, NACHRICHTEN aus Chemie, Technik und Laboratorium, 31, 798 (1983).

"Theoretical Studies of Polyvinyl-Substituted Carbenium and Silylenium Ions," T. Truong, M. S. Gordon, and P. Boudjouk, Organometallics, 3, 484 (1983).

"New Approaches to the Synthesis of Novel Organosilanes," P. Boudjouk, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original objectives of this program were: (a) to investigate the applicability of electrosynthetic methods to the synthesis of novel organosilanes and reactive intermediates containing silicon and (b) to develop further the use of Lewis acids to synthesize a wide variety of simple and complex organosilanes. During the course of these efforts a third area of research, the acceleration of chemical reactions using ultrasonic waves, was undertaken.

The electrochemical studies have resulted in the first time characterization of a wide variety of functionalized silanes using cyclic voltammetry and pulse polaragraphy. These functionalities include chlorosilanes, bromosilanes, iodosilanes, alkoxy- and aryloxysilanes as well as acetoxysilanes. Additionally, we have examined a number of silicon dihalides by these techniques. These compounds are characterized by high reduction potentials, approximately -3.0v vs. $Ag/AgClO_4$ (0.01M), and irreversible reductions. Some substituent effects were noted: vinyl, phenyl and hydro tend to make a chlorosilane easier to reduce.

The most important developments were along the lines of electrosynthesis. We have been able to couple chlorosilanes at a mercury electrode at controlled potential producing silicon-silicon bonds. The technique is difficult and flawed by the requirements that the system be free of oxygen and water. Typical reaction conditions employed a batch cell configuration but we have recently utilized a flow cell apparatus with good success.

Our efforts on Lewis Acid catalyzed reactions of organosilanes led to the synthesis of a number of simple silacycloalkanes in good yields from alpha-omega bis(trimethylsilyl)substituted alkanes. The cyclization process was found to be quite efficient, producing 60-85% yields of silacycloalkane product. The facile synthesis of a complex cage system such as 1-silaadamantane by this technique suggests that Lewis Acids may be very effective in performing organized redistribution reactions on organosilanes.

Early in this program we became involved in investigating the effects of ultrasonic waves on the course of chemical reactions. This was more or less an accidental occurrence as result of a need for some prototype compounds we were investigating by electrochemistry. In brief, we have found that ultrasonic waves from a simple sonic cleaning bath greatly accelerate a wide variety of reactions, especially reactions that involve metals.

We have examined over a dozen different "classical" organic reactions and found that ultrasonic waves not only shorten reaction time compared to the same reaction conducted at room temperature in the absence of sonic waves but also permit some reactions to be conducted under the mild conditions of a sonic bath (30-40°C and atmospheric pressure) that normally require more rigorous conditions.

In addition to the obvious benefit of running reactions at lower temperatures and pressures, we have also found that very often the yields are significantly higher and the product distribution simpler when the reaction is run in the presence of sonic waves than when run under the "normal" conditions of high temperature and/or high pressure.

The consequences of a lower energy requirement and cleaner reactions with higher yields are apparent and for this reason the potential for more widespread use of ultrasonic waves in synthesis is considerable. Commercialization of this technique is more than a faint possibility. Several companies have undertaken serious efforts to apply sonic waves to some of their processes.

COMPLETED PROJECT SUMMARY

TITLE: Effect of Toluene on the Solubility of Biohazardous Volatile Synthetic Organic Compounds

PRINCIPAL INVESTIGATOR: Professor Ervin Hindin
Civil and Environmental Engineering
Washington State University
Pullman, WA 99164

INCLUSIVE DATES: 1 June 1983 - 31 May 1984

GRANT NUMBER: AFOSR-83-0175

COSTS AND FY SOURCE: $11,999, FY 83 (Mini Grant)

PUBLICATION:

"Effect of Toluene on the Solubility of Biohazardous Volatile Synthetic Organic Compounds," Ervin Hindin, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The principal aim of this study was to determine the changes in mobility of three known carcinogenic organic compounds, benzene, 1,1,2 trichloroethylene and p-cresol, in aqueous systems containing dissolved toluene.

The solubility of toulene, benzene, 1,1,2 trichloroethylene and p-cresol singly in high purity water at 20°C was determined under dynamic and static conditions. Solubility equilibrium under dynamic conditions was attained within 24 hours. At that time, toulene, benzene, 1,1,2 trichloroethylene, and p-cresol were found to be present in concentrations of 517 mg/l, 1736 mg/l, 1014/l, and 17.85 g/l respectively. While under static conditions the same four compounds were present at solubility concentrations of 519.6 mg/l, 1725 mg/l, 1045 mg/l, and 18.1 gl/l respectively. The time required to attain solubility equilibrium at a 10 cm depth for toluene was 168 hrs at a rate of 3.6 mg/l/hr and for benzene it was 1288 hrs at a rate of 6.1 mg/l/hr. The time it took for 1,1,2 trichloroethylene to reach solubility equilibrium at a 4.5 cm depth was 216 hrs at a rate of 4.8 hrs and for p-cresol it was 36 hrs at a rate of 5.3 g/l rate.

Toluene present in an aqueous solution enhanced the benzene solubility, decreased the time for solubility to be attained and increased the rate at which solubility was attained. Toluene present in the water caused little difference in the time for 1,1,2 trichloroethylene to reach solubility equilibrium, but caused a more rapid rate in attaining solubility equilibrium and increased the solubility equilibrium concentration. The effect of toluene on the solubility kinetics of p-cresol was to reduce the time in attaining solubility equilibrium, increase the rate in achieving solubility equilibrium and caused little change in the solubility concentration.

Order of desorption of benzene, 1,1,2 trichloroethylene and p-cresol from a soil saturated with the three organic compounds by an aqueous toulene solution followed the magnitude of the polarity of the compounds being eluted. The sequence of removal was benzene followed by 1,1,2 trichloroethylene. Para cresol did not elute from the soil due to probable chemical bonding and/or strong physical attraction forces.

COMPLETED PROJECT SUMMARY

TITLE: Structural and Synthetic Organosilicon Chemistry

PRINCIPAL INVESTIGATOR: Professor Michael E. Jung
Department of Chemistry
University of California, Los Angeles
Los Angeles, CA 90024

INCLUSIVE DATES: 1 July 1981 - 30 June 1984

GRANT NUMBER: AFOSR-81-0185

COSTS AND FY SOURCE: $50,472, FY 81; $54,583, FY 82; $59,049, FY 83

SENIOR RESEARCH PERSONNEL: Dr. T. W. Newton
Dr. L.-M. Zeng

JUNIOR RESEARCH PERSONNEL:

G. L. Hatfield
J. A. Hagenah
L. A. Light
P. K. Lewis

PUBLICATIONS:

"Total Synthesis of Isopavine and Intermediates for the Preparation of Substituted Amitriptyline Analogues: Facile Routes to Substituted Dibenzocyclooctatrienes and Dibenzocycloheptatrienes," M. E. Jung and S. J. Miller, J. Am. Chem. Soc., 103, 1984 (1981).

"Use of Silyloxydienes in Synthesis. Total Syntheses of the Sesquiterpene (±)-Seychellene," M. E. Jung, C. A. McCombs, Y. Takeda, and Y.-G. Pan, J. Am. Chem. Soc., 103, 6677 (1981).

"Preparation of Iodoallylic Alcohols via Hydrostannylation: Spectroscopic Proof of Structures," M. E. Jung and L. A. Light, Tetrahedron Letters, 3851 (1982).

"Novel Oxidative Rearrangement of α, β- Unsaturated Ketone Hydrazones on Iodination in Base," M. E. Jung and G. L. Hatfield, Tetrahedron Letters, 3991 (1982).

"Addition of Organocuprates to Aldehydes via their Trimethylsilyl Iodide Adducts," M. E. Jung and P. Lewis, Synth. Commun., 13, 213 (1983).

"Synthesis of Syn-7-benzyloxy-4-methylbicyclo-[2.2.1]hept-5-en-2-one, an Intermediate for the Synthesis of Steroids and Tricothecanes; Tandem Anionic [1,3]-[3,3] Sigmatropic Rearrangement," M. E. Jung and G. L. Hatfield, Tetrahedron Letters, 2931 (1983).

"Facile Synthesis of (3aS)- 1,3a-Dimethyl-2,3,3a,5,6,7-hexahydroinden-4(5H)-one, an Intermediate for Sterold Synthesis," M. E. Jung and G. L. Hatfield, Tetrahedron Letters, 3175 (1983).

"Simple, Stereospecific Preparation of Z-3-Iodoacrylic Acid from Propiolic Acid and Methylmagnesium Iodide," M. E. Jung, J. A. Hagenah, and L.-M. Zeng, Tetrahedron Letters, 3973 (1983).

"Reaction of Oximes with Trimethylsilyl Iodide: Dehydration and Beckmann Rearrangement," M. E. Jung and L.-M. Zeng, Tetrahedron Letters, 933 (1983).

"Structural and Synthetic Organosilicon Chemistry," M. E. Jung, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

We have carried out numerous new synthetic transformations using organosilicon chemistry. Treatment of substituted phenylacetaldehydes with trimethylsilyl iodide (TMSI) afforded a quantitative yield of the oxygen-bridged dibenzocyclooctadiene. From this compound, we were able to prepare the alkaloid isopavine and substituted intermediates for the synthesis of amitriptyline analogues in very high overall yield. We developed a route to both cyclic and acyclic 2-silyloxydienes and investigated their use in Diels-Alder cycloadditions. In particular we used this method in two total syntheses of the tricyclic sesquiterpene seychellene. Several studies on the preparation of vinyl iodides were also carried out. Using tributyltin hydride, propargylic alcohols were easily converted into the trans or cis vinyl iodides in high yield and with good stereoselectivity. The iodination of ketone hydrazones in the presence of base was also investigated as a method for forming vinyl iodides. We discovered an intriguing rearrangement of β,γ-unsaturated ketone hydrazones under these conditions which affords additional evidence for a cationic mechanism for this iodination. The addition of organocuprate reagents to -iodoalkyl trimethylsilyl ethers (formed from aldehydes and TMSI) produced secondary alcohols in good yield. A study on the preparation of substituted hydrindane derivatives for the synthesis of steroids was also carried out. An optically active vinyl iodide which could serve as an AB-ring synthon and a hydrindanone model for the CD-ring system were synthesized. A final preparation of vinyl iodides was carried out; addition of methylmagnesium iodide to propiolic acid produced Z-3-iodoacrylic acid in high yield. Finally, the use of trimethylsilyl iodide (TMSI) for dehydration of aldoximes and Beckman rearrangement of aryl ketoximes was studied. Several other structural and synthetic projects have been begun but are not yet finished.

COMPLETED PROJECT SUMMARY

TITLE: Synthesis of a Series of Acetylene Terminated Olegomers: Structure Property Relationships

PRINCIPAL INVESTIGATOR: Professor James J. Kane
Department of Chemistry
Wright State University
Dayton, OH 45435

INCLUSIVE DATES: 1 April 1983 - 31 March 1984

GRANT NUMBER: AFOSR-83-0123

COSTS AND FY SOURCE: $12,000, FY 83 (Mini Grant)

PUBLICATION:

"Synthesis of a Series of Acetylene Terminated Olegomers: Structure Property Relationships," James J. Kane, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The initial goals of this project included synthesis of a series of bis-acetylene terminated aryl ether sulfone monomers and oligomers, their cure, and thermal evaluation of the cured materials.

Key intermediates for the synthesis of a series of four bis-acetylene aryl ether sulfones were synthesized. The intermediates were the oligomeric bis-phenols resulting from nucleophilic aromatic substitution of 4,4'-dichlorodiphenyl sulfone with an excess of the salts of each of the following bis-phenols: 2,2-di-(di-hydroxyphenyl)perfluoropropane (IV), 4,4'-dihydroxybenzophenone (V), 4,4'-dihydroxydiphenyl ether (VI), and 4,4'-dihydroxydiphenyl methane (VII).

Two of the resulting oligomeric bis-phenols (those arising from IV and VI) were converted to bis aryl bromides by the Ullman ether synthesis with excess amounts of m-dibromobenzene.

COMPLETED PROJECT SUMMARY

TITLE: Polyphosphorus Compounds Containing Phosphorus-Nitrogen Bonds

PRINCIPAL INVESTIGATOR: Professor R. Bruce King
Department of Chemistry
University of Georgia
Athens, GA 30602

INCLUSIVE DATES: 1 January 1981 - 31 December 1983

GRANT NUMBER: AFOSR-81-0051

COSTS AND FY SOURCE: $63,470, FY 81; $70,180, FY 82; $82,325, FY 83

SENIOR RESEARCH PERSONNEL: Dr. N. D. Sadanani
Dr. P. N. Kapoor
Dr. P. M. Sundaram

JUNIOR RESEARCH PERSONNEL: K. S. RaghuVeer
W. -K. Fu
M. J. Greene

PUBLICATIONS:

"Novel Diisopropylamino Derivatives of Trivalent Phosphorus," R. B. King, N. D. Sadanani, and P. M. Sundaram, Chem. Comm., 477 (1983).

"New Dialkylamino Derivatives of Trivalent Phosphorus," R. B. King, N. D. Sadanani, and P. M. Sundaram, Phosphorus and Sulfur, in press.

"Bis(dialkylamino)phosphines," R. B. King and P. M. Sundaram, J. Org. Chem., submitted.

"Polyphosphorus Compounds Containing Phosphorus-Nitrogen Bonds," R. B. King, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original scientific objective of this basic research program was the understanding of the synthesis and chemical reactivity of organic compounds consisting of a carbon backbone containing several bis(dialkylamino)phosphino substituents, $(R_2N)_2P$. This class of organophosphorus compounds, which has received very little attention, is of potential importance as intermediates in the manufacture of materials of possible value to the Air Force in diverse applications including antioxidants, lubricity agents, elastomers, flame retardants, and fuel cell catalysts.

The development of methods for the synthesis of organic compounds bearing several $(R_2N)_2P$ substituents requires the availability of important dialkylaminophosphorus building blocks. In this connection major effects of the size of the dialkylamino group on the resulting dialkylaminophosphorus chemistry were documented for the first time. Thus much of the

originally planned chemistry failed when dimethylamino substituents were present owing to the sensitivity of such systems towards strong reducing agents (e.g., lithium and magnesium metals) which frequently led to the conversion of essentially all of the dimethylamino groups to $(Me_2N)_3P$. However, much interesting new dialkylaminophosphorus chemistry was developed by using larger dialkylamino groups. Thus the compounds $(Et_2N)_2PH$ and $(iPr_2N)_2PH$ were found to be isolable whereas we have been unable to isolate or even detect $(Me_2N)_2PH$ using analogous methods. Similarly the cyclotetraphosphines $(iPr_2N)_4P_4$ and $(Cx_2N)_4P_4$ (Cx = cyclohexyl) are isolable and $(Et_2N)_4P_4$ has tentatively been detected whereas we have not yet been able to isolate or even detect the analogous $(Me_2N)_4P_4$ using similar methods. Other achievements from this research project include the isolation of the first $(R_2N)(R'O)PH$ derivatives (i.e., R = isopropyl, R' = methyl, ethyl, isopropyl, and tert-butyl), the detection of the first R_2NPH_2 derivatives containing hydrocarbon R groups (i.e., R = cyclohexyl or isopropyl or R_2N = 2,2,6,6-tetramethylpiperidino), the first preparation of a ditertiary phosphine of the type $(R_2N)_2PCH_2CH_2P(NR_2)_2$ by the base-catalyzed addition of an $(R_2N)_2PH$ derivative to $(R_2N)_2PCH{=}CH_2$, and the development of some metal carbonyl chemistry of $(iPr_2N)_2PH$.

symbols

COMPLETED PROJECT SUMMARY

TITLE: Mechanisms and Kinetics of Diphthalocyanine Electrode Processes. Electrochemistry of Rare-Earth Diphthalocyanines

PRINCIPAL INVESTIGATOR: Dr. M. M. Nicholson
Member of Technical Staff
Rockwell International Science Center
Anaheim, CA 92803

INCLUSIVE DATES: 1 May 1980 - 30 April 1984

CONTRACT NUMBERS: F49620-80-C-0060 and F49620-83-C-0088

COSTS AND FY SOURCE: $30,000, FY 80; $60,259, FY 81; $66,222, FY 82; $60,594, FY 83; $37,073, FY 84

JUNIOR RESEARCH PERSONNEL: F. A. Pizzarello
T. P. Weismuller

PUBLICATIONS:

"Kinetics of Color Reversal in Lutetium Diphthalocyanine Oxidation Products Formed with Different Anions," F. A. Pizzarello and M. M. Nicholson, J. Electrochem. Soc., 128, 1288 (1981).

"Multicolor Electrochromic Display Technology," M. M. Nicholson and T. P. Weismuller, Proc. IEEE 1983 National Aerospace and Electronics Conf., Vol. 1 (1983).

"Electrochromic Flat-Panel Multicolor Displays," M. M. Nicholson, Information Display, 4, (Feb 84).

"The Role of Oxygen in the Redox Chemistry of Lutetium Diphthalocyanine," M. M. Nicholson and T. P. Weismuller, J. Electrochem. Soc., 131, 2311 (1984).

"Electrochromics," M. M. Nicholson, Encyclopedia of Materials Science and Engineering, M. B. Bever, Ed., Pergamon, New York (in press).

"Mechanisms and Kinetics of Diphthalocyanine Electrode Processes," M. M. Nicholson, T. P. Weismuller, and F. A. Pizzarello, Final Technical Report, Contract F49620-80-C-0060.

"Electrochemistry of Rare-Earth Diphthalocyanines," M. M. Nicholson and T. P. Weismuller, Final Technical Report, Contract F49620-83-C-0088.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Thin films of the lanthanide diphthalocyanines undergo a series of redox reactions that are accompanied by pronounced changes in the visible absorption spectra. In this project, transient and equilibrium

characteristics of lutetium diphthalocyanine were investigated by electrochemical and direct chemical techniques in combination with optical absorption spectroscopy. The objective was to establish reaction stoichiometries and rate data pertaining to the electrochromic processes.

Further detail was reported on the slow reversion of anodically oxidized lutetium diphthalocyanine films to the green state on standing in moist air. The first-order rate constants, ranging from $< 0.003\ h^{-1}$ to $0.1\ h^{-1}$, depended on the counter anion present in the oxidized film. Although vacuum-sublimed films of the dye could be rapidly oxidized or reduced electrochemically, their responses to dissolved chemical oxidizing agents, including aqueous Fe^{3+}, Br_2, Cl_2, and Ce^{4+}, were slow, requiring seconds to minutes for completion. However, such direct chemical reactions were accelerated by electrochemical precycling or by pretreatment of the film with a surfactant. Both pretreatments appeared to increase the porosity of the film and, hence, its permeability to counter ions required for the redox reactions. Cyclic color switching of the dye by the indirect coulometric technique was also demonstrated.

It was found by absorption spectroscopy that oxygen reacted irreversibly with a vacuum-sublimed lutetium diphthalocyanine film, probably converting it, in the presence of water vapor, from $LuPc_2$ to $LuHPc_2^+O_2^-$, where Pc represents the phthalocyaninato group $C_{32}H_{16}N_8$. A closely related, but reversible, reaction with oxygen occurred with the dye dissolved in acidified dimethylformide. This information accounted for apparent anomalies in the behavior of rare-earth diphthalocyanines reported from several laboratories and permitted formulation of a consistent redox scheme including at least five oxidation states of the dye.

In the final contract year, series of equilibrium potentials were determined for lutetium diphthalocyanine electrode films in HCl, tetrabutylammonium chloride (TBACl), and KCl-TBACl electrolytes near 25°C. Absorption spectra were used to identify the condition of equilibrium after application of a potential step and to determine the extent of conversion between consecutive oxidation, or color, states. At 50% conversion, equilibrium potentials were correlated with pH and pCl through simple forms of the Nernst equation. At conversions other than 50%, major deviations from the anticipated Nernst expression occurred. These effects were consistent with exchange of several complexing ions and/or solvent molecules between the oxidized and reduced members of each couple.

COMPLETED PROJECT SUMMARY

TITLE: Basic Research in Novel Inorganic Reagents and Fluorocarbon Chemistry

PRINCIPAL INVESTIGATOR: Dr. Carl J. Schack
Dr. Karl O. Christe
Rocketdyne Division
Rockwell International
Canoga Park, CA 91304

INCLUSIVE DATES: 4 March 1981 - 30 September 1984

CONTRACT NUMBER: F49620-81-C-0020

COSTS AND FY SOURCE: $49,999, FY 81; $72,783, FY 82; $74,721, FY 83
$72,743, FY 84

PUBLICATIONS:

"New Syntheses of Pentafluorotellurium Hypochlorite," C. J. Schack and K. O. Christe, J. Fluorine Chem., 21, 393 (1982).

"Synthesis and Characterization of TeF_5OF," C. J. Schack, W. W. Wilson, and K. O. Christe, Inorg. Chem., 22, 18 (1983).

"Reactions of Azidotrifluoromethane with Halogen Containing Oxidizers, C. J. Schack and K. O. Christe, Inorg. Chem., 22, 22 (1983).

"Reactions of Pentafluorotellurium Hypohalites with Fluoroolefins, C. J. Schack and K. O. Christe, J. Fluorine Chem., 24, 467 (1984).

"Synthesis of Bis-Pentafluorotelluriumoxide Fluorocarbons," C. J. Schack and K. O. Christe, J. Fluorine Chem., 26, 19 (1984).

"An Improved Synthesis of TeF_5OF," C. J. Schack and K. O. Christe, Inorg. Chem., 23, 2922 (1984).

"Sulfur Chloride Pentafluoride," C. J. Schack, R. D. Wilson, and M. W. Warner, Inorganic Syntheses, in press.

"Chlorine Fluorosulfate," C. J. Schack and R. D. Wilson, Inorganic Syntheses, in press.

"Bis-Pentafluorotelluriumoxide Fluorocarbons," C. J. Schack and K. O. Christe, J. Fluorine Chem., in press.

"Reactions of TeF_5OCl with Fluorocarbon Iodides," C. J. Schack and K. O. Christe, J. Fluorine Chem., in press.

"Synthesis of Pentafluoroseleniumoxide Fluorocarbons," C. J. Schack and K. O. Christe, J. Fluorine Chem., to be published.

"Basic Research in Novel Inorganic Reagents and Fluorocarbon Chemistry," C. J. Schack and K. O. Christe, Final Technical Report.

PATENT APPLICATIONS AND DISCLOSURES:

"Pentafluorotellurium Hypofluorite," C. J. Schack, W. W. Wilson, and K. O. Christe.

"Pentafluorotelluriumoxide Fluorocarbons," C. J. Schack and K. O. Christe.

"Multi-(TeF_5O)- Substituted Fluorocarbons," C. J. Schack and K. O. Christe.

"An Improved Process for Preparing TeF_5OF," C. J. Schack and K. O. Christe.

"Oxidation of Fluorocarbon Iodides with Pentafluorotellurium Hypochlorite and Derivatives Thereof," C. J. Schack and K. O. Christe.

"Pentafluoroselenium Oxide Fluorocarbons," C. J. Schack and K. O. Christe.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of this program was the development of stable, high-density fluorocarbons suitable for applications such as flotation liquids in gyros. Selected for this goal were TeF_5O- and SeF_5O- substituents. An improved, practical synthesis of TeF_5OH was developed and two new routes were discovered for its direct conversion to TeF_5OCl in excellent yield. The previously unknown TeF_5OF was discovered and characterized, and later a much improved synthesis was found which eliminated the use of a dangerous reagent. Both of these hypohalites added across olefinic double bonds forming novel TeF_5O- substituted fluorocarbons. Some of these addition reactions gave isomeric products. Employment of $Xe(OTeF_5)_2$ in reactions with fluoroolefins resulted in the high yield formation of novel bis- and tetrakis- TeF_5O substituted derivatives from mono and diolefins, respectively. These included aliphatic perfluoro-, chloro-, and hydrogen containing olefins as well as cyclic ones. The incorporation of Cl and H substituents into the fluorocarbons was found to enhance the reactivity of these olefins relative to the perfluoro analogues (C_2F_4 being an exception). Reactions of TeF_5OF and $Xe(OTeF_5)_2$ with fluoroaromatics gave various TeF_5O- substituted cyclohexenes and cyclohexadienes. Fluorocarbon iodides were oxidized at low temperature using TeF_5OCl resulting in $R_fI(OTeF_5)_2$ adducts. UV radiation induced or thermal decomposition of the primary fluorocarbon iodo derivatives led to the formation of R_fOTeF_5 in a previously unknown pathway.

All of the TeF_5O- substituted fluorocarbons prepared are colorless gases or liquids of low volatility and are thermally stable. Density measurements on the $R_f(OTeF_5)_n$ compounds show that the TeF_5O- group contributes nearly as much as iodine and appreciably more than bromine to the density of fluorocarbons.

Analogous reactions of $Xe(OSeF_5)_2$ with fluoroolefins gave low yields of the novel bis SeF_5O- substituted compounds. The main products were new mono SeF_5O- substituted species and epoxides.

The reaction of azidotrifluoromethane with halogen oxidizers was found to give new N-halo, N-fluorosulfato amines. These compounds were characterized.

COMPLETED PROJECT SUMMARY

TITLE: Structural and Dynamic Studies of Materials Possessing High Energy Content

PRINCIPAL INVESTIGATOR: Professor Nicholas J. Turro
Department of Chemistry
Columbia University
New York, NY 10027

INCLUSIVE DATES: 1 November 1980 - 31 October 1983

GRANT NUMBER: AFOSR-81-0013

COSTS AND FY SOURCE: $102,373, FY 80; $105,392, FY 81; $108,990, FY 82

SENIOR RESEARCH PERSONNEL:

Dr. N. P. Hacker
Dr. J. Bolt
Dr. T. A. Jenny
Dr. M. A. Paczkowski
Dr. T. Okubo
Dr. I. R. Gould
Dr. G. F. Lehr
Dr. C.-J. Chung
Dr. G. S. Cox

JUNIOR RESEARCH PERSONNEL:

D. A. Hrovat
X. Li
B. H. Baretz
M. B. Zimmt
G. C. Weed
C.-H. Tung
P. Hauptman

PUBLICATIONS:

"Photoreactions of Biacetyl and Tetramethylethylene. Solvent and Temperature Effects," N. J. Turro, K. Shima, C.-J. Chung, C. Tanielian, and S. Kanfer, Tetrahedron Letters, 21, 2775 (1980).

"Chemiluminescent Thermolysis of Alpha-Peroxylactones," N. J. Turro and M.-F. Chow, J. Am. Chem. Soc., 102, 5058 (1980).

"Organic Photochemistry: The Laser vs. the Lamp. The Behavior of Diphenylcarbene Generated at High Light Intensities," N. J. Turro, M. Aikawa, J. A. Butcher, Jr., and G. W. Griffin, J. Am. Chem. Soc., 102, 5127 (1980).

"Quenching of Chemiexcited Acetone Phosphorescence by Aryl Alkyl Ketones. A Search for Electronic Effects," M. F. Mirbach, V. Ramamurthy, M. J. Mirbach, N. J. Turro, and P. J. Wagner, Nouveau J. de Chemie, 4, 471 (1980).

"Chemical Generation of Excited States," N. J. Turro and V. Ramamurthy, Rearrangements in Ground and Excited States, Vol. 3, P. deMayo, Ed., Academic Press, New York, NY (1980).

"Quenching of the Fluorescence of 2-Norboranone and Derivatives by Electron-Rich and Electron-Poor Ethylenes," N. J. Turro and G. Farrington, J. Am. Chem. Soc., 102, 6051 (1980).

"Photoinduced Oxetane Formation Between 2-Norboranone and Derivatives with Electron-Poor Ethylenes, N. J. Turro and G. Farrington, J. Am. Chem. Soc., 102, 6056 (1980).

"Practical Synthesis of Semibullvalene," N. J. Turro, J.-M. Liu, H. E. Zimmerman, and R. E. Factor, J. Org. Chem., 45, 3511 (1980).

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"Reaction of Singlet Oxygen with Trans-Cyclooctene. Evidence for a 1,2-Dioxetane Intermediate," Y. Inoue and N. J. Turro, Tetrahedron Letters, 21, 4327 (1980).

"Quenching of Acetone Triplets by 1,3-Dienes in Fluid Solution," N. J. Turro and Y. Tanimoto, J. Photochem., 14, 199 1980.

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"Micelles, Magnets, and Molecular Mechanisms. Application to Cage Effects and Isotope Separation," N. J. Turro, Pure and Appld. Chem., 53, 259 (1981).

"An Efficient, High Conversion Photoinduced Emulsion Polymerization. Magnetic Field Effects on Polymerization Efficiency and Polymer Molecular Weight," N. J. Turro, M.-F. Chow, C. J. Chung, and C.-H. Tung, J. Am. Chem. Soc., 102, 7391 (1980).

"Natural Correlation Diagrams. A Unifying Theoretical Basis for Analysis of n Orbital Initiated Ketone Photoreactions," B. Bigot, A. Devacquet, and N. J. Turro, J. Am. Chem. Soc., 103, 6 (1981).

"Photochemistry of 2,3-Dimethylcyclobutanone. Temperature and Wavelength Effects," N. J. Turro, D. Bauer, V. Ramamurthy, and F. Warren, Tetrahedron Letters, 22, 611 (1981).

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"Time Resolved Laser Flash Spectroscopic Study of Benzyl Radical Pairs in Micellar Cages," N. J. Turro, M.-F. Chow, D.-J. Chung, Y. Tanimoto, and G. C. Weed, J. Am. Chem. Soc., 103, 4574 (1981).

"Measurement of Rate Processes of Free Radicals in Homogeneous and Micellar Solutions by CIDNP," G. F. Lehr and N. J. Turro, Tetrahedron, 37, 3411 (1981).

"Generation Diffusivity and Quenching of Singlet Oxygen in Polymer Matrices Investigated via Chemiluminescence Methods," N. J. Turro, M.-F. Chow, and M. Blaustein, J. Phys. Chem., 85, 3014 (1981).

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"Radical Pair Reactions in Micellar Solution in the Presence and Absence of Magnetic Fields," N. J. Turro, J. Mattay, and G. F. Lehr, Inorganic Reactions in Organized Media, S. L. Holt, Ed., ACS Symposium Series 177, Washington, D.C.

"The Laser vs. the Lamp. A Novel Laser-Induced Adiabatic Reaction and Luminescence of Benzophenone," N. J. Turro, M. Aikawa, and I. R. Gould, J. Am. Chem. Soc., 103, 856 (1982).

"Laser Flash Spectrometric Investigations of Biradicals and Caged Radical Pairs," N. J. Turro, Tetrahedron Lett., 38, 809 (1982).

"Solvent and Deuterium Isotope Effects on the Lifetime of Singlet Oxygen Determine by Direct Emission Spectroscopy at 1.27 um," T. A. Jenny and N. J. Turro, Tetrahedron Letters, 2923 (1982).

"Influence of Nuclear Spin on Chemical Reactions: Magnetic Isotope and Magnetic Field Effects (A Review)," N. J. Turro, Proc. National Acad. Sci. USA, 80, 609 (1983).

"Remarkable Inhibition of Oxygen Quenching of Phosphorescence by Complexation with Cyclodextrins," N. J. Turro, S. G. Cox, and X. Li, Photochem. Photobio., 37, 149 (1983).

"Absolute Rate Constants for Decarbonylation of Phenylacetyl and Related Radicals," N. J. Turro, I. R. Gould, and B. H. Baretz, J. Phys. Chem., 87, 531 (1983).

"Magnetic Field and Magnetic Isotope Effects on Photoinduced Emulsion Polymerization," N. J. Turro, M.-F. Chow, D.-J. Chung, and C.-H. Tung, J. Am. Chem. Soc., 105, 1572 (1983).

"Micellar Systems as 'Supercages' for Reactions of Geminate Radical Pairs. Magnetic Effects," N. J. Turro, and G. C. Weed, J. Am. Chem. Soc., 105, 1961 (1983).

"Application of Weak Magnetic Fields to Influence Rates and Molecular Weight Distributions of Sytrene Polymerization," N. J. Turro, Industrial and Engineering Chemical Product Research and Development, 22, 272 (1983).

"Stereochemistry of Photoinitiated Emulsion Polymerization," N. J. Turro, I. F. Pierola, and C.-J. Chung, J. Polymer. Sci., 21, 1085 (1983).

"Structural and Dynamic Studies of Materials Possessing High Energy Content," N. J. Turro, Final Technical Report.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A major goal of the research supported by this grant has been the advancement of our fundamental knowledge of the nature and properties of materials possessing an exceptionally high energy content. Such knowledge should be valuable for the development of novel chemical lasers, for the development of novel and effective approaches for the protection of polymers against oxidative degradation and for the development of methods to improve structural properties of polymer systems.

The research explored during this project summary period has been highlighted by the elucidation of photochemical mechanisms through the use of time resolved laser flash spectroscopy. Carbenes, radical pairs, ylides, singlet molecular oxygen and other high energy species have been investigated in detail. The first detailed and systematic determination of the absolute rate constants for the addition of carbenes to ethylenes was accomplished. The application of weak magnetic fields for controlling the reactivity of radical pairs in colloidal systems was discovered and explored. The ability of weak magnetic fields to dramatically influence the rate and molecular weights in emulsion polymerization was demonstrated.

RESEARCH EFFORTS COMPLETED IN FY 84

COMPLETED PROJECT SUMMARIES - ATMOSPHERIC SCIENCES

LT COL GERALD J. DITTBERNER
LT COL TED S. CRESS
MAJOR JAMES I. METCALF (USAF Reserve)

High Time Resolution Studies of the Auroral Ionosphere AFOSR-82-0093	John C. Foster Center for Atmospheric and Space Sciences Utah State University Logan, UT 84332
Stochastic Theory of Multiple Light Scattering in Clouds AFOSR-MIPR-84-00007 AFOSR-MIPR-83-00048	Dan T. Gillespie Naval Weapons Center China Lake, CA 93555
High Frequency Radar Studies of the Very High Latitude Ionosphere AFOSR-ISSA-83-00039 AFOSR-ISSA-84-00042	Raymond A. Greenwald Applied Physics Laboratory The Johns Hopkins University Laurel, MD 20707
A Survey of High-Latitude Ionospheric Electron Content and Scintillation-Producing Irregularities using EISCAT AFOSR-81-0049, AFOSR-83-0054	J. K. Hargreaves Dept. of Environmental Sciences University of Lancaster Lancaster, England
Ionic Reactions in the Earth's Upper Atmosphere AFOSR-83-0177	Thomas M. Miller Dept. of Physics and Astronomy University of Oklahoma Norman, OK 73019
A Study of the Effects of Triggered Lightning AFOSR-82-0206	Charles B. Moore Dept. of Physics N. Mexico Inst. of Mining & Tech. Socorro, NM 87801
High Time Resolution Thermospheric Temperature and Wind Studies in the Arctic AFOSR-80-0240	G. G. Sivjee Geophysical Institute University of Alaska Fairbanks, AK 99701

COMPLETED PROJECT SUMMARY

TITLE: High Time Resolution Studies of the Auroral Ionosphere

PRINCIPAL INVESTIGATOR: Dr. John C. Foster
Center for Atmospheric and Space Sciences
Utah State University
Logan, UT 84332

INCLUSIVE DATES: 1 Feb. 1982 - 31 May 1984

GRANT NUMBER: AFOSR-82-0093

COSTS AND FY SOURCE: $52,490, FY 82; $83,665, FY 83

SENIOR RESEARCH PERSONNEL: Dr. J. R. Doupnik

PUBLICATIONS:

"An Empirical Electric Field Model Derived from Chatanika Radar Data," J. C. Foster, J. Geophys. Res., 88, 981 (1983).

"Mapping the Electrostatic Potentials from the Ionosphere to the Magnetosphere," J. J. Sojka, J. C. Foster, P. M. Banks, and J. R. Doupnik, Planet. Space Sci., 31, 1329 (1983).

"Multistation Measurements of High-Latitude Ionospheric Convection," R. A. Heelis, J. C. Foster, O. de la Beaujardiere, and J. Holt, J. Geophys. Res., 88, 10111 (1983).

"Ionospheric Signatures of Magnetospheric Convection," J. C. Foster, J. Geophys. Res., 89, 855 (1984)

"MITHRAS: A Brief Report," O. de la Beaujardiere et al., Radio Sci., 19, 655 (1984).

"High-Resolution Observations of Electric Fields and F Region Plasma Parameters in the Cleft Ionosphere," J. C. Foster, J. M. Holt, J. D. Kelly, and V. B. Wickwar, Proc. NATO Advanced Workshop on the Morphology and Dynamics of the Polar Cusp, J. Holtet, Ed., D. Reidel, Dordrecht (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An experimental technique to provide high-resolution radar observations of the spatial structure of the high-latitude ionosphere was developed. Prototype azimuth scanning experiments with the incoherent scatter radar at Chatanika, Alaska, were conducted during the winter of 1981-1982. Analysis software was developed to permit spatial mapping of ionospheric density, temperature, and convection electric field over a 1000-km radius field of view around the radar. The initial experiments provided details of the spatially complex region near local midnight at auroral latitudes. Patches of high-density F region plasma were observed to be convected

equatorward out of the night sector polar cap, from whence they were caught up in the sunward convective flow away from midnight at auroral latitudes. The convection pattern can be uniform over several thousand kilometers longitudinally at dusk and dawn, but the effects of equatorward transport from polar latitudes dominate the observations near midnight.

The technique has been merged with AFOSR-supported efforts at Millstone Hill, Massachusetts, and applied in coordinated experiments using the incoherent scatter radars at Sondre Stromfjord, Greenland, and Millstone Hill. Participation in the Magnetosphere-Ionosphere-Thermosphere Radar Studies (MITHRAS) data analysis included several multi-instrument studies of the large-scale high-latitude convection pattern. A near-simultaneous picture of the electric field pattern in one hemisphere was realized in these studies. An empirical high-latitude convection electric field model was derived from the Chatanika observations and presented in a numerical format for ease of inclusion in ionospheric and magnetospheric mapping simulations. Comparison of radar-derived electric field data with ionospheric models was directed at fine-tuning the model parameters for improved predictive capability.

COMPLETED PROJECT SUMMARY

TITLE: Stochastic Theory of Multiple Light Scattering in Clouds

PRINCIPAL INVESTIGATOR: Dr. Dan T. Gillespie
Code 3807
Naval Weapons Center
China Lake, CA 93555

INCLUSIVE DATES: 1 April 1983 - 30 September 1984

INSTRUMENT NUMBER: AFOSR-MIPR-83-00048, AFOSR-MIPR-84-00007

COSTS AND FY SOURCE: $20,000, FY 83; $40,000, FY 84

PUBLICATIONS:

"A Stochastic Calculation of Multiply-Scattered Lidar Returns," D.T. Gillespie, Air Force and Navy Sci. and Engrg. Symp., Norfolk Naval Air Station, 14-16 Nov 1984.

"Stochastic-Analytic Approach to the Calculation of Multiply Scattered Lidar Returns," D. T. Gillespie, J. Optical Soc. Amer. A, 2, 1307 (1985).

"Analytic Reduction of the Monostatic Lidar Multiple Backscattering Integral," D. T. Gillespie, NWC Tech. Publ. 6605 (1985).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The investigation was based on transmission of a short, highly collimated pulse of laser radiation at time t=0 into a well-mixed cloud of particles with known light scattering and absorption properties. The objective was to develop a reliable method for calculating the intensity $J_n(t)$ of backscattered radiation having undergone exactly n scatterings in the cloud. The approach taken to calculating $J_n(t)$ was unusual for an analytic approach in that it was based not on the radiative transfer equation but on the premise that the laser pulse consists of a collection of propagating photons that are scattered and absorbed by the cloud particles in a probabilistic manner. Considerable effort was devoted to providing a quantitative physical rationale for this point of view. The calculation of the related probability function P_n was easy for n=1 but much more difficult for n greater than 1. The key to this calculation is the Random Variable Transformation Theorem, a powerful but little-known result in the theory of random variables. Application of this theorem allowed derivation of an exact but highly formal integral expression for P_n. This expression was reduced to a computable form which yielded an expression for $J_n(t)$ in the form of an explicit (3n-4)-dimensional integral of a bounded integrand over the unit cube. Evaluation of this integral by means of Monte Carlo techniques for a cloud of isotropically scattering particles yielded results accurate to better than 1% for n ranging from 2 to 6 and for a full range of receiver aperture angles. From these numerical results, formulas valid for very small receiver apertures were deduced, and for the special case of n=2 an exact analytical formula was obtained. These new results not only are interesting in their own right but also augur well for the further utility of this "stochastic-analytic" approach.

COMPLETED PROJECT SUMMARY

TITLE: High Frequency Radar Studies of the Very High Latitude Ionosphere

PRINCIPAL INVESTIGATOR: Dr. Raymond A. Greenwald
Applied Physics Laboratory
The Johns Hopkins University
Laurel MD 20707

INCLUSIVE DATES: 15 Feb 83 - 30 Sep 84

GRANT NUMBER: AFOSR-ISSA-83-00039, AFOSR-ISSA-84-00042 to National Science Foundation

COSTS AND FY SOURCE: $25,000, FY 83; $35,000, FY 84

SENIOR RESEARCH PERSONNEL:

Dr. K.B. Baker

JUNIOR RESEARCH PERSONNEL:

R.A. Hutchins
C. Hanuise
A.D.M. Walker
P.F. Bythrow
T.A. Potemra

PUBLICATION:

"High-Frequency Radiowave Probing of the High-Latitude Ionosphere," R.A. Greenwald, Johns Hopkins APL Technical Digest, 6, 38 (1985)

"An HF Phased-Array Radar for Studying Small-Scale Structure in the High-Latitude Ionosphere," R.A. Greenwald, K.B. Baker, R.A. Hutchins and C. Hanuise, Radio Sci. 20, 63 (1985).

"Drift Motions of Very High Latitude F-region Irregularities: Azimuthal Doppler Analysis," C. Hanuise, R.A. Greenwald and K.B. Baker, J. Geophys. Res., 90, 9717 (1985)

"A Case Study of Plasma Processes in the Dayside Cleft," K.B. Baker, R.A. Greenwald, A.D.M. Walker, P.F. Bythrow, T.A. Potemra, D. Hardy, F. Rich, and C. Rino, J. Geophys. Res. (submitted for publication, 1984)

"Determination of the Fluctuation Level of Ionospheric Irregularities from Radar Backscatter Measurements," A.D.M. Walker, R.A. Greenwald, and K.B. Baker, Radio Sci. (Submitted for publication, 1985).

"HF Radar Observations of Pulsations near the Magnetospheric Cusp," A.D.M. Walker, R.A. Greenwald, and K.B. Baker, J. Geophys. Res. (submitted for publication, 1985).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Under joint funding by National Science Foundation, AFOSR, Air Force Geophysics Laboratory, Defense Nuclear Agency, and Rome Air Development Center, a high-frequency radar was built at the AFGL field site in Goose Bay, Labrador, to observe ionospheric irregularity structure and to perform collaborative ionospheric investigations with the incoherent scatter radar at Sondre Stromfjord, Greenland. The radar operates within the frequency range 8-20 MHz and with peak power up to 125 W.

F-region irregularity structures were found to drift toward geomagnetic west with speeds approaching 2 km/sec during the afternoon but to follow a curved trajectory that was predominantly westward at the lowest latitudes in the late evening. The Doppler spectra of the afternoon F-region irregularities were found to be quite narrow, in contrast to the broader spectra of irregularities in the E-region. The mean Doppler velocity derived from the radar data is used to construct two-dimensional maps of the irregularity drift, under conditions of approximate uniformity of the drift within the radar field of view. Simultaneous observations by the Goose Bay radar and the HILAT satellite have been used to study the plasma and irregularities in the vicinity of the dayside cleft. The data indicated that both the medium-scale irregularities associated with scintillation measurements and the small-scale irregularities that produce radar backscatter are colocated in space in a region of low-energy electron precipitation which produces a sharp poleward gradient in the F-region plasma density. The plasma drift appears to have a poleward component in this region and thus the plasma is subject to the F-region gradient-drift instability. On the poleward edge of the cleft the plasma drift is antiparallel to the density gradient, tending to stabilize the plasma and possibly accounting for the limited latitudinal extent of both the medium-scale and small-scale irregularity regions.

An attempt to compare drift velocity measurements by the Goose Bay radar with those of the Sondre Stromfjord and Millstone Hill radars was initiated. Preliminary results are encouraging, although some practical problems of scanning mode and spatial separation of the observations require further effort.

Comparision of summer and winter observations by the Goose Bay radar have revealed a seasonal variation in the diurnal occurrence of F-region irregularities. In winter, irregularities are observed typically in the noon through midnight local time sector, whereas in summer they are observed almost exclusively during hours of high solar zenith angle. This variation may be related to enhancement of the E-region conductivity by solar extreme ultraviolet (EUV) radiation, but the mechanism is not understood at present. A continuing effort is planned to address these and other issues emerging from the present research.

COMPLETED PROJECT SUMMARY

TITLE: A Survey of High-Latitude Ionospheric Electron Content and Scintillation-Producing Irregularities using EISCAT

PRINCIPAL INVESTIGATOR: Dr. J. K. Hargreaves
Dept. of Environmental Sciences
University of Lancaster
Lancaster, England

INCLUSIVE DATES: August 1981 - 30 April 1983

GRANT NUMBERS: AFOSR-81-0049, AFOSR-83-0054

COSTS AND FY SOURCE: $17,000, FY 83 (Prior funding data unavailable)

SENIOR RESEARCH PERSONNEL: Dr. S. C. Kirkwood

PUBLICATION:

"EISCAT Electron Density Studies (Second Year)," S. C. Kirkwood and J. K. Hargreaves, AFGL-TR-83-0165, Air Force Geophysics Laboratory (1983).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research was undertaken in collaboration with the Space Physics Division of the Air Force Geophysics Laboratory and was jointly funded by the U.S. Army Research, Development, and Standardization Group in the U.K. A series of measurements was undertaken using the European Incoherent Scatter (EISCAT) radar facility at Tromso, Norway, to document irregularities of electron density in the ionospheric F region. Measurements using the EISCAT common programs were made from August 1981 to January 1982 and from April 1982 to January 1983. Measurements using a high-time-resolution rapid scanning program developed by the University of Lancaster were made in December 1981, June 1982, September 1982, and November/December 1982. Large-amplitude localized electron density enhancements were observed in active night-time conditions. Two types of large-scale enhancement were observed. One was characterized by large amplitudes in the E and lower F region, with amplitudes decreasing rapidly with further increase in altitude. The other was confined to the F region with largest amplitudes on the topside. Evidence was also found for intermediate-scale structuring associated with precipitation, in some instances, and with probable formation by plasma instabilities in others. Significant problems remain with the derivation of ion drift velocities, and further investigation of these problems should have high priority. The rapid-scanning measurements can resolve small scale structures, and, once the accuracy of drift velocity determination is improved, these measurements may provide detailed information on the structure of large and intermediate scale electron density enhancements.

COMPLETED PROJECT SUMMARY

TITLE: Ionic Reactions in the Earth's Upper Atmosphere

PRINCIPAL INVESTIGATOR: Dr. Thomas M. Miller
Dept. of Physics and Astronomy
University of Oklahoma
Norman, OK 73019

INCLUSIVE DATES: 1 May 1983 - 31 January 1984

GRANT NUMBER: AFOSR-83-0177 (Mini-grant)

COSTS AND FY SOURCE: $11,954, FY 83

PUBLICATION:

"Temperature Dependence of the Ion-Molecule Reactions $N^+ + CO$, $C^+ + NO$, and C^+, CO^+, $CO_2^+ + O_2$ from 90-450 K," T. M. Miller, R. E. Wetterskog, and J. F. Paulson, J. Chem. Phys., 80 (No. 10), 4922 (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Several ion-molecule reactions were studied by means of measurements with the Selected-Ion Flow Tube (SIFT) at the Air Force Geophysics Laboratory. The results illustrated the temperature dependence of the rate coefficients from 90 to 450 K. Favorable agreement was determined in comparison to previous measurements at particular temperatures. A study of the perturbation of the gas flow in the tube by high-speed helium injectors led to a redesign of the injector to eliminate a shock wave in the tube. A related apparatus was built at the University of Oklahoma for the study of ion-ion reactions, and preliminary measurements for the reaction of Cl_2^+ and Cl^- have been made. Improvements to the measurement techniques have been identified for implementation in future studies of these reactions.

COMPLETED PROJECT SUMMARY

TITLE: A Study of the Effects of Triggered Lightning

PRINCIPAL INVESTIGATOR: Prof. Charles B. Moore
Dept. of Physics
New Mexico Institute of Mining and Technology
Socorro, NM 87801

INCLUSIVE DATES: 15 May 1982 - 31 December 1983

GRANT NUMBER: AFOSR-82-0206

COSTS AND FY SOURCE: $27,269, FY 82

SENIOR RESEARCH PERSONNEL: C. R. Holmes
P. Hubert (Centre d'Etudes Nucleaires de Saclay, France)

JUNIOR RESEARCH PERSONNEL: D. N. Holden
I. J. Caylor
D. L. Hall

PUBLICATIONS:

"Characteristics of French Ruggieri Antihail Rockets Used to Trigger Lightning," C. B. Moore, I. J. Caylor, D. L. Hall, and T. F. Stueber, Measurement Note 27, NMIMT (Nov 82).

"Triggered Lightning at Langmuir Laboratory in July-August 1982," P. Hubert, Institut de Recherche Fondamentale, Division de la Physique (Nov 82).

"Characteristics of American Rockets Used for Triggering Lightning," C. B. Moore, D. L. Hall, I. J. Caylor, T. F. Stueber, B. Cason, and D. Patrick, Measurement Note 29, NMIMT (Feb 84).

"Triggered Lightning in France and New Mexico," P. Hubert, Endeavor, New Series, 8 (No. 2), 85 (1984).

"Triggered Lightning in New Mexico," P. Hubert, P. Laroche, A. Eybert-Berard, and L. Barret, J. Geophys. Res., 89 (No. D2), 2511 (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A joint research program was undertaken among New Mexico Institute of Mining and Technology, Flight Hazards Branch of the Air Force Flight Dynamics Laboratory, and the French Commissariat a l'Energie Atomique for the purposes of evaluating techniques for triggering lightning, measuring lightning currents, and investigating effects of discharges on clouds and precipitation. During July and August 1982, 17 of 31 launches of rockets towing wires successfully triggered lightning discharges. Resulting

currents ranged from a few hundred amperes to 79 kA. The experimental results showed that lightning can be triggered reliably when negatively charged clouds overhead produce an electric field strength of more than 9 kV/m at the surface. A grounded wire must then be injected into the subcloud region at a vertical speed in excess of 100 m/sec (the drift velocity of positive ions under these ambient conditions) to a height in excess of 150m. The small rockets used in this investigation appear to be capable of triggering lightning more easily than those used previously for this purpose.

An 11-cm wavelength radar was built for the study of the interaction of lightning with precipitation. Limited data acquired in 1983 showed variations of radar echo reflectivity attributable to lightning. The radar will be used subsequently to investigate the hypothesis that lightning discharges greatly increase the coalescence efficiency of water drops, leading to local increases in precipitation rate.

COMPLETED PROJECT SUMMARY

TITLE: High Time Resolution Thermospheric Temperature and Wind Studies in the Arctic

PRINCIPAL INVESTIGATOR: Dr. G. G. Sivjee
Geophysical Institute
University of Alaska
Fairbanks, AK 99701

INCLUSIVE DATES: 1 August 1980 - 29 September 1984

GRANT NUMBER: AFOSR-80-0240

COSTS AND FY SOURCE: $49,959, FY 80; $87,090, FY81; $74,953, FY 82; $32,956, FY 83

SENIOR RESEARCH PERSONNEL: Dr. Gerald J. Romick (PI until 29 Sept 1983)
Dr. T. Hallinan
J. Baldridge

JUNIOR RESEARCH PERSONNEL: S. A. Smith
R. J. Sica

PUBLICATIONS:

"High Time Resolution Intensified Images of 6300A Fabry-Perot Fringes Applied to Auroral Thermospheric Studies," G. J. Romick, T. J. Hallinan, G. G. Sivjee, and G. Hernandez, IAGA Bulletin, 45, 291 (1981).

"Investigation of Clear Air Turbulence Using the Poker Flat MST Radar," S. A. Smith, M. S. Thesis, University of Alaska (1982).

"Verification of WSFO Fairbanks Sigmets of Moderate or Greater Turbulence with Poker Flat MST Radar for the Period September 8, 1980, through March 31, 1981," S. A. Smith and R. R. Hoopes, Technical Attachment to Borealis Briefs, Natl. Wea. Serv. (Jan 82).

"The Observation of Shear-Induced Turbulence by the Poker Flat MST Radar," S. A. Smith, G. J. Romick, and K. Jayaweera, Spring Meeting, Amer. Geophys. Union (1982).

"Lower Thermosphere Neutral Winds and Temperatures in the Auroral Zone," T. J. Hallinan, G. Hernandez, G. J. Romick, G. G. Sivjee, and R. Sica, EOS, Trans. Amer. Geophys. Union, 63, 392 (1982).

"Upper Thermosphere Neutral Winds and Temperatures in the Auroral Zone Derived from the [OI] 630 nm Emission," G. J. Romick, G. G. Sivjee, R. G. Roble, and G. Hernandez, EOS, Trans. Amer. Geophys. Union, 63, 392 (1982).

"Thermospheric Wind Measurements in the Auroral Zone," R. Sica, M. H. Rees, G. J. Romick, G. G. Sivjee, G. Hernandez, and G. R. Swenson, EOS, Trans. Amer. Geophys. Union, 63, 392 (1982).

"An Experimental Picture of the High Latitude E and F Regions," R. Sica, M. H. Rees, G. J. Romick, G. Hernandez, and R. T. Tsunoda, EOS, Trans. Amer. Geophys. Union, 63, 1051 (1982).

"Lower Thermospheric Dynamics in the Auroral Region near Fairbanks, Alaska," G. Hernandez, R. Sica, G. J. Romick, V. B. Wickwar, and R. T. Tsunoda, IAGA Meeting, Hamburg, Germany (1983).

"Auroral Zone Thermospheric Winds near Solar Minimum," G. Hernandez, J. L. Smith, R. G. Roble, T. L. Killeen, R. Sica, and G. J. Romick, EOS, Trans. Amer. Geophys. Union, 65, 250 (1984).

"An Equal Noise Spectroscopic Measurement," G. Hernandez, R. J. Sica, and G. J. Romick, Appl. Opt., 23, 915 (1984).

"Auroral Zone Thermospheric Dynamics Using Fabry-Perot Interferometric Measurements of the OI 15867K Emission," R. Sica, Ph. D. Thesis, University of Alaska (1984).

"Examination of a Type Red Aurora with Radar, Optics, and Theoretical Modeling," V. B. Wickwar, W. Kofman, M. Rees, R. Sica, G. Romick, G. Hernandez, and S. Mende, XXI General Assembly, Intl. Union Radio Sci., Florence, Italy (1984).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research program was initiated to develop state-of-the-art instrumentation to study the dynamics of the polar thermosphere with high time resolution. The technique involves the measurement of Doppler profiles as well as wavelength shifts in various optical emissions to study the upper and lower thermosphere. Initially, a low light level television system (image orthicon) was coupled to a 150 mm aperture Fabry-Perot index-of-refraction scanning system. Acquisition of aurorally associated fringes in fractions of a second were obtained. However, lack of electronic stability in older systems of this type precludes the routine analysis of the data. A subsequent attempt to use a solid state intensified CID television camera indicated promise, but the lack of sensitivity limited high time resolution data to very bright events. Rather than continue this direction, emphasis was switched to obtaining high quality temperature and wind measurements in the index-of-refraction scanning mode simultaneously in the upper and lower thermosphere. This was coupled with the installation and operation of a new piezo-electric rapid scanning system to assist in the investigation of thermospheric neutral (6300 OI) and ion (7320 OII) and D-Region (OH) dynamics. The piezo-electric interferometor was constructed at the NOAA Aeronomy Laboratory under AFOSR support.

The initial results show the presence of gradients and divergences in the winds in both the high and low thermosphere in response to magnetic activity. From 44 nights of data collected prior to spring 1983, the dynamical behavior has been investigated both on individual nights and as a statistical average. In general on individual nights westward drifting auroral forms accompany the westward evening zonal wind. The arrival of the westward electrojet heralds the change from westward to eastward zonal flow, with time delays from less than 15 minutes to over 2 hours.

Increasing electrojet strength results in higher zonal wind speeds. Near magnetic midnight, as the aurora moves east, the equatorward meridional wind decreases in velocity. Vertical winds are commonly observed and can be quite large and variable, particularly during periods associated with pulsating aurora. Statistically the general flow pattern is poleward and westward in the evening changing to southward and eastward in the morning. With increasing geomagnetic activity the change in direction occurs earlier in magnetic local time, and the meridional wind pattern shifts equatorward along with the auroral oval. Consequently the average wind pattern in the north during low geomagnetic activity is similar to the average in the south during moderate activity. The average thermospheric temperature is governed by the geomagnetic activity and is related to the previous day's 10.7 cm solar flux. The increase in temperature with solar flux is about the same as with auroral activity (225 K). The piezo-electric system provided a number of additional nights (40) of 6300 OI wind data during the spring and fall of 1984 with much better time resolution than any heretofore obtained. Those data are being analyzed in continuing studies with various thermospheric models of atmospheric dynamics.